

- The rearrangement from one structure is expected to the other structure if the ligand steric hindrance is present in the complex. Steric hindrance between ligands can be reduced by converting a cubic into a square antiprismatic arrangement.
- Square Antiprismatic coordination environments occur in $[\text{Zr}(\text{acac})_4]$ (d^0) and in the anions in the salts $\text{Na}_3[\text{TaF}_8]$ (d^0), $\text{K}_2[\text{ReF}_8]$ (d^1) and $\text{K}_2[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3][\text{Nb}(\text{ox})_4]$ (d^1). Always keep in mind that, specifying the counter-ion is important since the energy difference between 8-coordinate structures tends to be small with the result that the preference between two structures may be altered by crystal packing forces in two different salts.
- Examples are seen in a range of salts of $[\text{Mo}(\text{CN})_8]^{3-}$, $[\text{W}(\text{CN})_8]^{3-}$, $[\text{Mo}(\text{CN})_8]^{4-}$ or $[\text{W}(\text{CN})_8]^{4-}$ which possess square antiprismatic or dodecahedral structures depending on the cation.
- Further examples of dodecahedral complexes include $[\text{Y}(\text{H}_2\text{O})_8]^{3+}$ and a number of complexes with didentate ligands: $[\text{Mo}(\text{O}_2)_4]^{2-}$ (d^0), $[\text{Ti}(\text{NO}_3)_4]$ (d^0), $[\text{Cr}(\text{O}_2)_4]^{3-}$ (d^1), $[\text{Mn}(\text{NO}_3)_4]^{2-}$ (d^5) and $[\text{Fe}(\text{NO}_3)_4]^-$ (d^5).
- The hexagonal bipyramid is a rare coordination environment, but may be favored in complexes containing a hexadentate macrocyclic ligand, for example $[\text{CdBr}_2(18\text{-crown-6})]$.
- A bicapped trigonal prism is another option for 8-coordination, but is only rarely observed, e.g. in $[\text{ZrF}_8]^{4-}$ (d^0) and $[\text{La}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (d^0).

c. Coordination number 9: -

- Coordination number 9 is also not very common in the coordination chemistry.
- The geometries associated with the CN 9 are *tricapped trigonal prismatic*
- The anions $[\text{ReH}_9]^{2-}$ and $[\text{TcH}_9]^{2-}$ (both d^0) provide examples of 9-coordinate species in which the metal centre is in a tricapped trigonal prismatic environment.
- A coordination number of 9 are most often associated with yttrium, lanthanum and the f-block elements.
- The tricapped trigonal prism is the only regular arrangement of donor atoms yet observed, e.g. in $[\text{Sc}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Y}(\text{H}_2\text{O})_9]^{3+}$ and $[\text{La}(\text{H}_2\text{O})_9]^{3+}$.

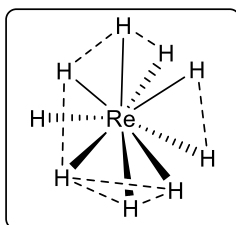


Figure 3.13: The structure of $[\text{ReH}_9]^{2-}$

d. Coordination number 10: -

- Coordination number 10 is generally observed in the f block elements having the oxidation state +3 e.g. $[\text{Th}(\text{ox})_4(\text{H}_2\text{O})_2]^{4-}$
- The higher coordination is generally impossible for d block elements because of their small size as it will result in the high steric crowding around the metal centre and this will destroy the stability of the complex.

e. Coordination number 12: -

- It is always dangerous to draw conclusions on the basis of the non-existence of structure types, but, from data available at the present time, it seems that a coordination of ≥ 10 is generally confined to the f-block metal ions.
- Coordination number 12 is also observed in the f block elements having the oxidation state +3

- An important example is $[\text{Ce}(\text{NO}_3)_6]^{2-}$ in which NO_3^- acts as a bidentate ligand. **Interestingly, if the metal size is small, NO_3^- acts as a monodentate ligand.** For instance, if we consider that, in this example also NO_3^- is acting as a monodentate ligand, there will be huge strain in the two donor atoms of the ligand and the complex becomes unstable. If the cation size increases, this hindrance becomes negligible and complex is stable.
- Complexes containing $[\text{BH}_4]^-$ and related ligands are an exception, e.g. in $[\text{Hf}(\text{BH}_4)_4]$ and $[\text{Zr}(\text{MeBH}_3)_4]$ the ligands are tridentate and the metal centers are 12-coordinate.

III. MORE ABOUT CN 4 AND CN 6

i. Valance Bond Theory for Tetrahedral complexes: -

Tetrahedral complexes are either sp^3 or sd^3 hybridized. Let us consider some of the examples of these types of hybridization-

- a. $[\text{NiCl}_4]^{2-}$: In this example, the central metal atom is Ni having the oxidation state as +2. The Ni^{2+} constitutes to the 3d^8 configuration. Since the Cl^- is the weak ligand, there is no any pairing of the electrons take place. And hence, due to this reason there is no any d orbital is remaining vacant to accept the pair of electrons. The chloride ion donates its electron pair to the one 4s and three 4p orbitals to give sp^3 hybridization. The magnetic study confirms that the complex is paramagnetic in nature due to presence of the unpaired electrons.

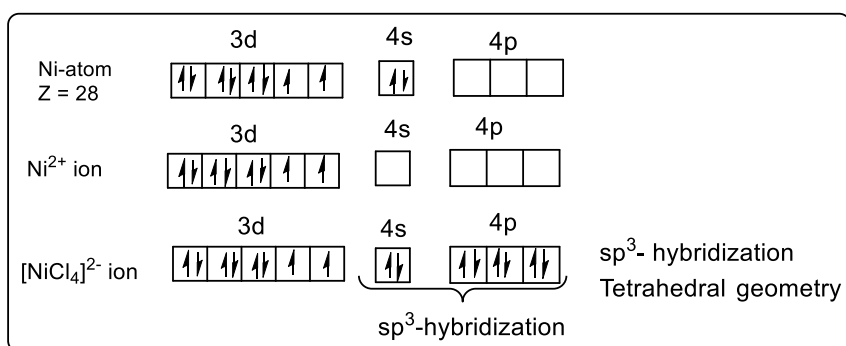


Figure 3.14: Hybridization of complex $[\text{NiCl}_4]^{2-}$

- b. $[\text{NiCO}_4]$: In this example, the central metal atom is Ni having the oxidation state as zero. The Ni^0 constitutes to the $3\text{d}^8 4\text{s}^2$ configuration. Since the CO is the strong ligand, there is pairing of the electrons take place. The two 4s^2 electrons shift to the 3d orbitals. And hence, due to this reason there is no any d orbital is remaining vacant to accept the pair of electrons. The carbonyl donates its electron pair to the one 4s and three 4p orbitals to give sp^3 hybridization. The magnetic study confirms that the complex is diamagnetic in nature due to absence of the unpaired electrons

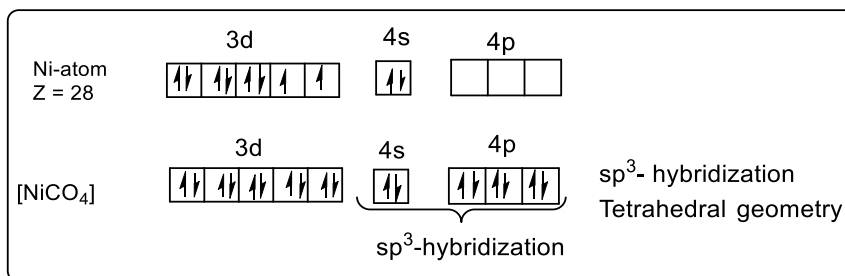
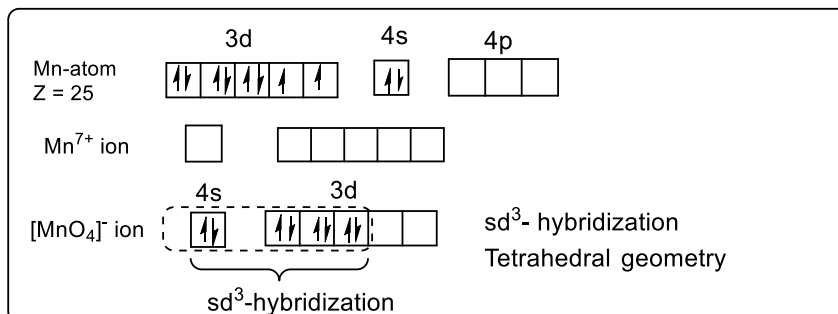
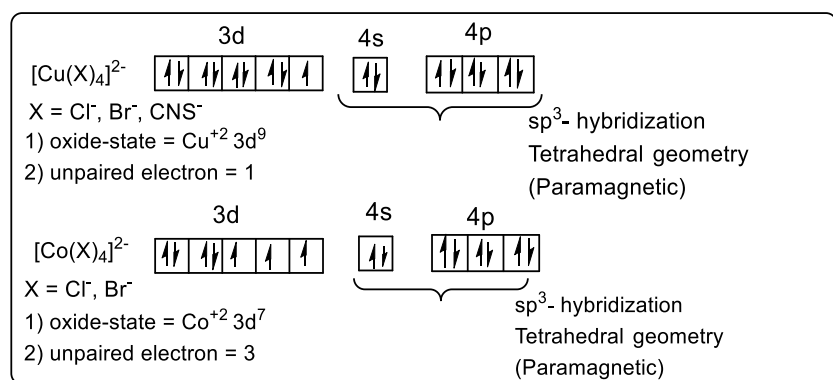
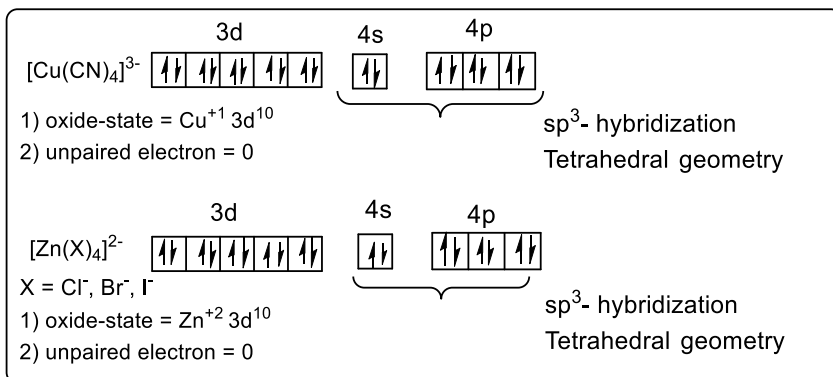


Figure 3.15: Hybridization of complex $[\text{NiCO}_4]$

- c. **[MnO₄]⁻**: In this example, the central metal atom is Mn having the oxidation state as +7. The Mn⁷⁺ constitutes to the 3d⁰ 4s⁰ configuration. There are all five d orbitals are remaining vacant to accept the pair of electrons. The oxygen donates its electron pair to the one s and three d orbitals hybridization to give sd³ hybridization. The magnetic study confirms that the complex is diamagnetic in nature due to absence of the unpaired electrons.

Figure 3.16: Hybridization of complex [MnO₄]⁻

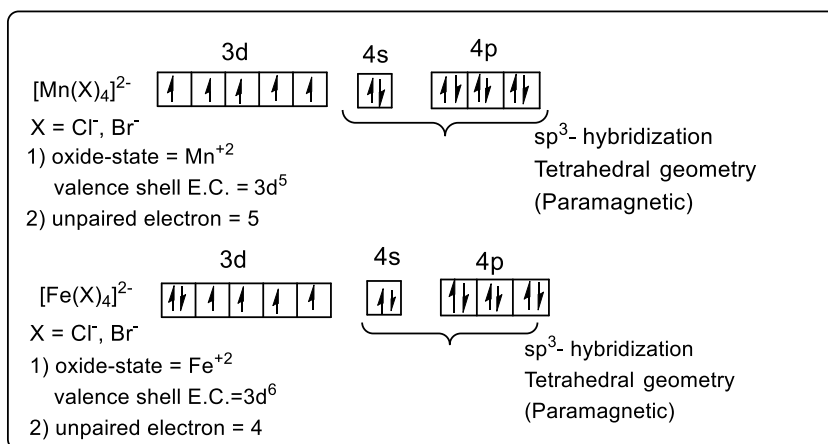


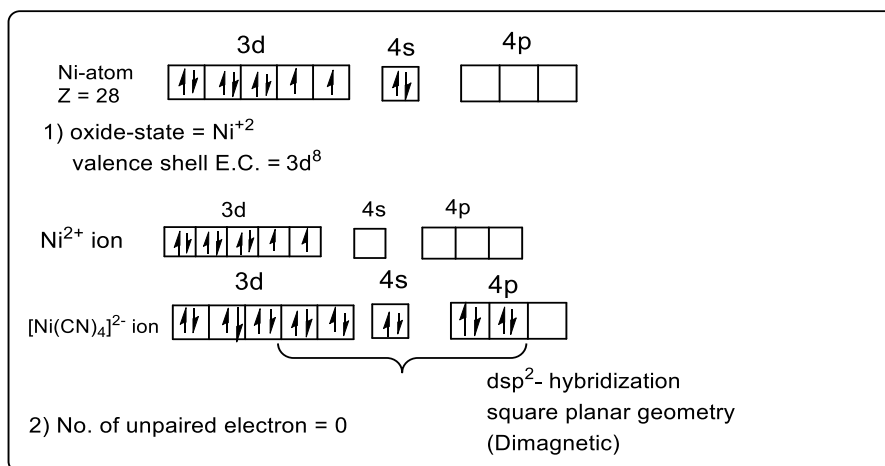
Figure 3.17: Hybridization of some of the tetrahedral complexes

ii. Valance Bond Theory for square planar complexes: -

Square planar complexes have the central metal cation in dsp² hybridization. The dsp² hybrid orbitals point towards the four corners of the square plane. Consider the following examples of the square planar complexes having the dsp² hybridization.

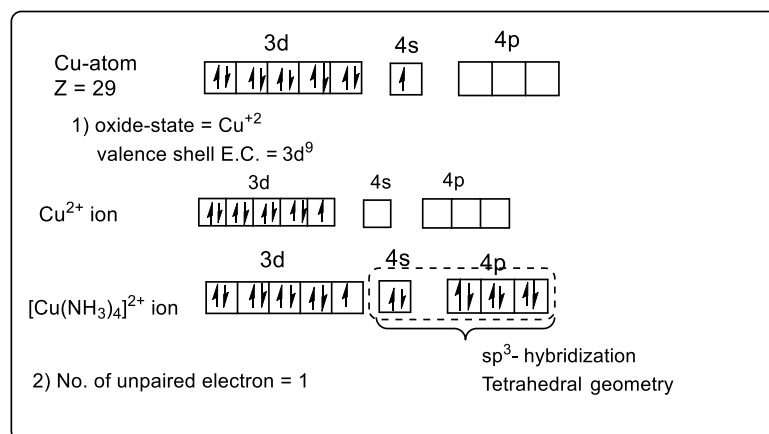
a. [Ni(CN)₄]²⁻:

In this example, the central metal atom is Ni having the oxidation state as +2. The Ni²⁺ constitutes to the 3d⁸ configuration. Since the CN⁻ is the strong ligand, there is pairing of the electrons take place. And hence, due to this reason there is one d orbital is remaining vacant to accept the pair of electrons. The cyanide ion donates its electron pair to the one 3d, one 4s and two 4p orbitals to give dsp² hybridization. The magnetic study confirms that the complex is diamagnetic in nature due to no presence of the unpaired electrons.

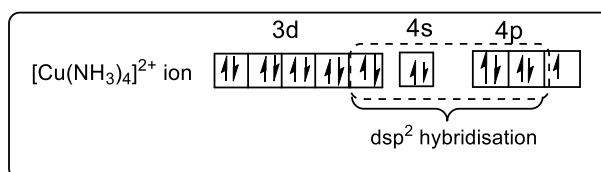
Figure 3.18: Hybridization of [Ni(CN)₄]²⁻

b. $[\text{Cu}(\text{NH}_3)_4]^{2+}$:

In this example, the central metal atom is Cu having the oxidation state as +2. The Cu^{2+} constitutes to the $3d^9$ configuration. There is no any possibility of pairing although the ammonia is the strong ligand, because there is only one unpaired electron in the d orbital. Thus instead of dsp^2 , it is expected to show sp^3 hybridization and should have tetrahedral structure instead of the square planar.

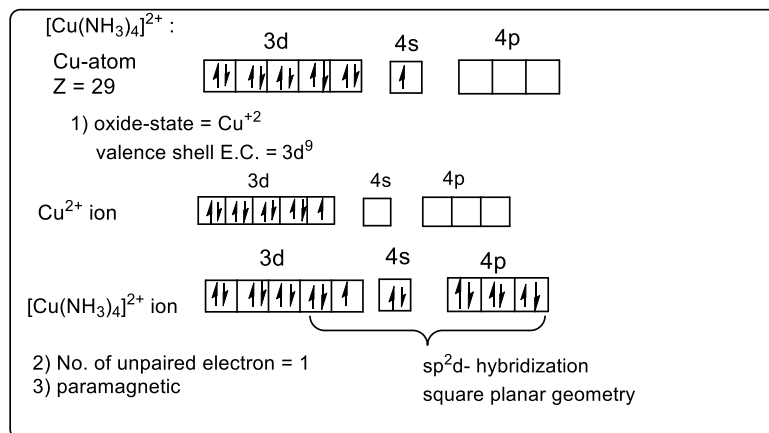
Figure 3.19: Proposed hybridization of $[\text{Cu}(\text{NH}_3)_4]^{2+}$

But ESR studies have confirmed that the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ has a square planar structure. Thus, to make the Cu^{2+} dsp^2 hybridized, it is considered that the one unpaired electron is promoted to the 4p orbital as shown below.



But later on it was also proved that this distribution of the electron is also not valid. Because if it is valid, the last electron having energy could have been lost easily and $[\text{Cu}(\text{NH}_3)_4]^{3+}$ could form easily but *this $[\text{Cu}(\text{NH}_3)_4]^{3+}$ doesn't even exist.*

Finally, Huggin suggested the correct square planar nature of this complex with the electron distribution as follows:

Figure 3.20: Actual hybridization of $[\text{Cu}(\text{NH}_3)_4]^{2+}$

iii. Valance Bond Theory for Octahedral complexes: -

Octahedral complexes are very interestingly explained on the basis of the valance bond theories. As stated in the earlier section, for Oh geometry, two types of the hybrdizations are possible - d^2sp^3 and sp^3d^2

The d orbital used for the d^2sp^3 hybridization is (n-1) d orbital which are inner d orbitals and hence these complexes are called as **inner orbital complexes** and on the other hand the d orbital used for the sp^3d^2 hybridization is (n) d orbital which are outer d orbitals and hence these complexes are called as **outer orbital complex**.

Generally, inner orbital complexes having hybridization d^2sp^3 are far more stable than that of the outer orbitals complexes which have hybridization sp^3d^2 but not always.

a. Inner orbital complexes

- i. **[Co(CN)₆]³⁻**: In this example, the central metal atom is Co having the oxidation state as +3. The Co^{3+} constitutes to the $3d^6$ configuration. Since the CN^- is the strong ligand, there is pairing of the electrons take place. And hence, due to this reason there is two d orbitals are remaining vacant to accept the pair of electrons. The cyanide ion donates its electron pair to the two 3d, one 4s and three 4p orbitals to give d^2sp^3 hybridization. The magnetic study confirms that the complex is diamagnetic in nature due to no presence of the unpaired electrons.

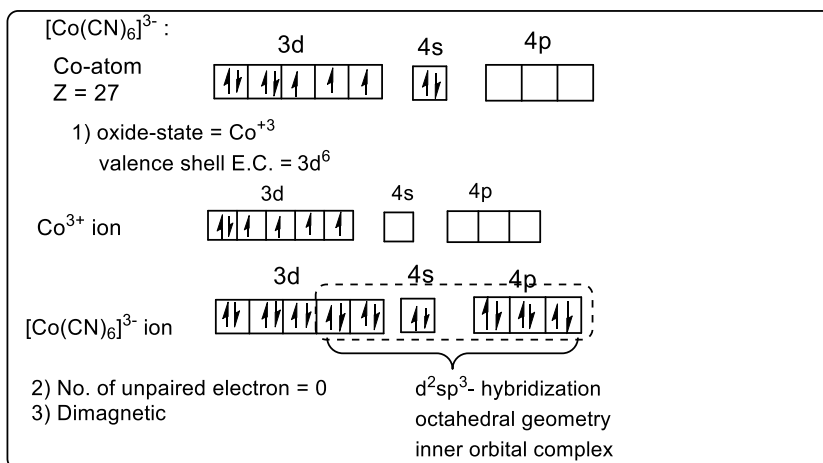
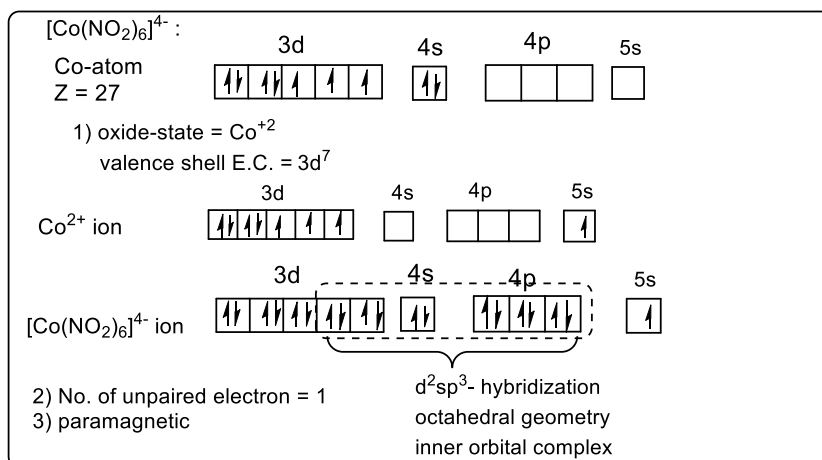
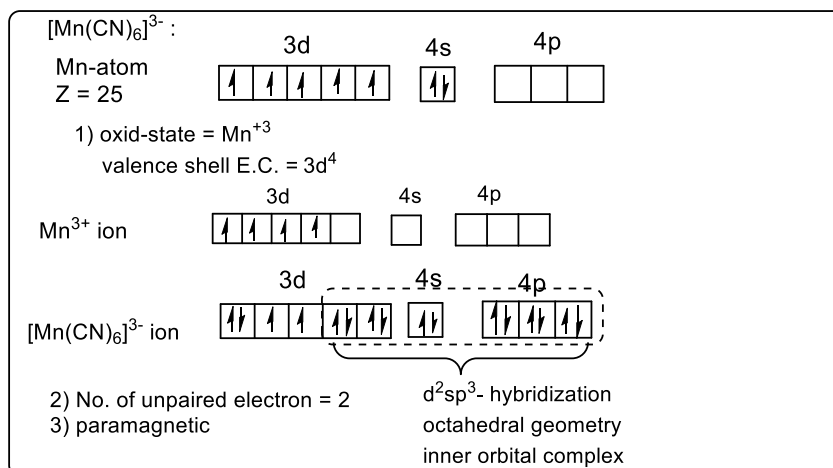


Figure 3.21: Hybridization of **[Co(CN)₆]³⁻**

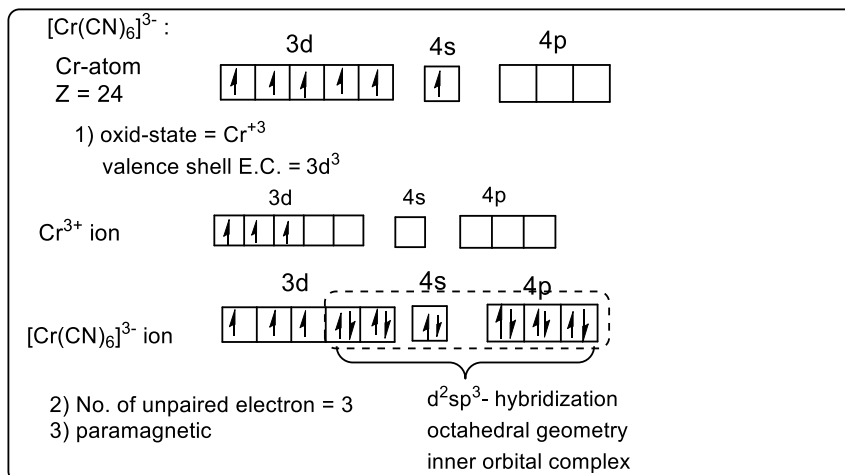
- ii. $[\text{Co}(\text{NO}_2)_6]^{4-}$: In this example, the central metal atom is Co having the oxidation state as +2. The Co^{2+} constitutes to the $3d^7$ configuration. Since the NO_2^- is the strong ligand, there is pairing of the electrons take place. Although after pairing, in last d orbital, there is one unpaired electron is remaining. Pauling suggested that, *two vacant 3d orbitals are made by exciting that one unpaired electron from 3d to 5s orbital*. This excitation of the electron to 5s orbitals was proved comprehensively. As the 5s orbitals are at high energy, the excited electron lost rapidly and metal gets oxidized easily. Complex $[\text{Co}(\text{NO}_2)_6]^{4-}$ gets oxidized easily to $[\text{Co}(\text{NO}_2)_6]^{3-}$ in the air and this proves that $[\text{Co}(\text{NO}_2)_6]^{4-}$ is very much unstable in the air due to excited 5s electrons. The magnetic study confirms that the complex is paramagnetic in nature due to presence of the unpaired electrons.

Figure 3.22: Hybridization of $[\text{Co}(\text{NO}_2)_6]^{4-}$

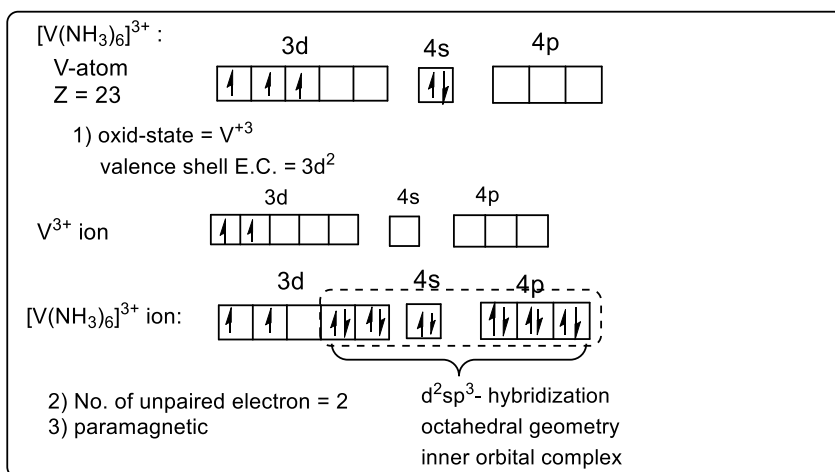
- iii. $[\text{Mn}(\text{CN})_6]^{3-}$: In this example, the central metal atom is Mn having the oxidation state as +3. The Mn^{3+} constitutes to the $3d^4$ configuration. Since the CN^- is the strong ligand, there is pairing of the electrons take place. Although pairing is there, two electrons are only paired leaving behind two electrons unpaired d orbital. If all unpaired electrons are paired, there would be violation of Hund's rule. And hence, after pairing all four electrons occupy the three d orbitals and two are left for the ligand donation. The magnetic study confirms that the complex is paramagnetic in nature due to presence of the unpaired electrons.

Figure 3.23: Hybridization of $[\text{Mn}(\text{CN})_6]^{3-}$

- iv. $[\text{Cr}(\text{CN})_6]^{3-}$: In this example, the central metal atom is Cr having the oxidation state as +3. The Cr^{3+} constitutes to the $3d^3$ configuration. The three electrons are occupied in three 3d orbitals leaving two vacant. Even though, the CN^- is the strong ligand, there is no pairing of the electrons take place. If three unpaired electrons are paired, there would be violation of Hund's rule. CN^- donates its electron pairs in the two remaining 3d orbitals yielding d^2sp^3 hybridization.

Figure 3.24: Hybridization of $[\text{Cr}(\text{CN})_6]^{3-}$

- v. $[\text{V}(\text{NH}_3)_6]^{3+}$: In this example, the central metal atom is V having the oxidation state as +3. The V^{3+} constitutes to the $3d^2$ configuration. The two electrons are occupied in two 3d orbitals leaving three vacant. Ammonia ligand donate its electron pairs in the two of the three remaining 3d orbitals yielding d^2sp^3 hybridization. *The important fact about this complex is that one 3d orbital remains vacant due to course of action.* These three orbitals degenerate and pairing doesn't take place even in the presence of the strong ligands. If two unpaired electrons are paired, there would be violation of Hund's rule. It is a paramagnetic complex due to presence of the unpaired electrons.

Figure 3.25: Hybridization of $[\text{V}(\text{NH}_3)_6]^{3+}$

Following chart shows some of the inner orbital complexes that shows sp^3d^2 hybridization:

Complex	Oxidation state of metal	Configuration	Ligand nature	Unpaired electrons
$[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$	+3	$3d^1$	Weak	1
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	+3	$3d^2$	Weak	2
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	+3	$3d^3$	Weak	3
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	+3	$3d^3$	Strong	3
$[\text{Cr}(\text{CN})_6]^{4-}$	+2	$3d^4$	Strong	2
$[\text{Mn}(\text{CN})_6]^{4-}$	+2	$3d^5$	Strong	1
$[\text{Fe}(\text{CN})_6]^{3-}$	+3	$3d^5$	Strong	1
$[\text{Fe}(\text{CN})_6]^{4-}$	+2	$3d^6$	Strong	0
$[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$	+2	$3d^6$	Both strong	0
$[\text{PtCl}_6]^{2-}$	+4	$3d^6$	Weak	0

Table 3.3: Hybridization of some of the inner orbital complexes that shows sp^3d^2 hybridization

b. Outer orbital complexes

- i. $[\text{CoF}_6]^{3-}$: In this example, the central metal atom is Co having the oxidation state as +3. The Co^{3+} constitutes to the $3d^6$ configuration. Since the F^- is the weak ligand, there is no such pairing of the electrons take place. And hence, due to this reason there is no d orbitals are remaining vacant to accept the pair of electrons. The fluoride ion donates its electron pair to the one 4s and three 4p, two 4d orbitals to give sp^3d^2 hybridization. The magnetic study confirms that the complex is paramagnetic in nature due to presence of the unpaired electrons.

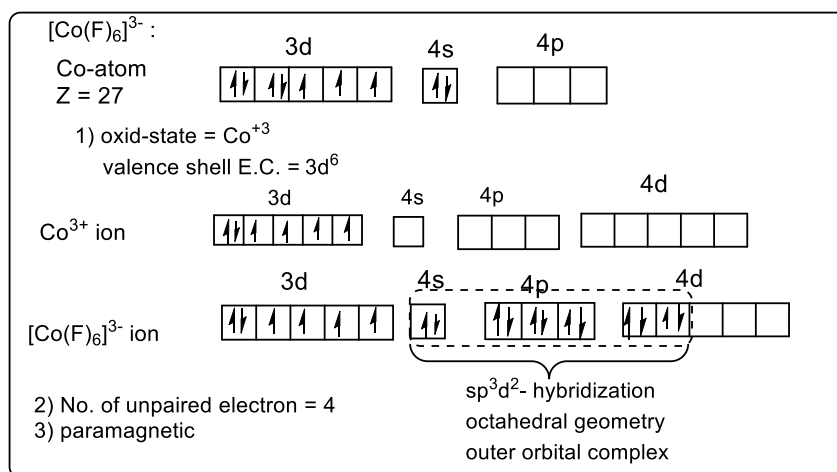
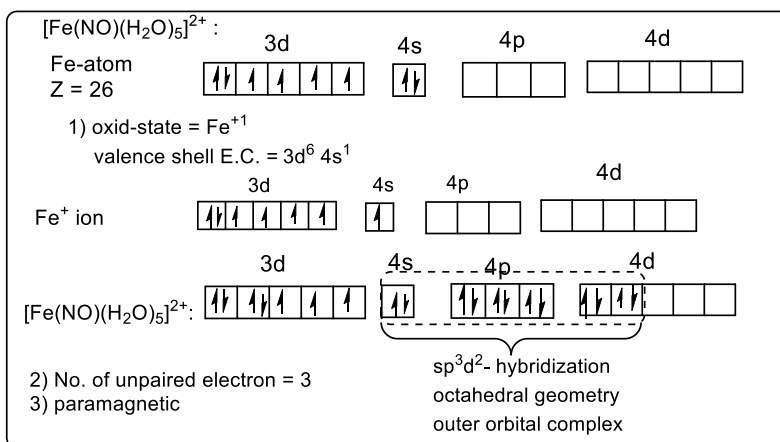


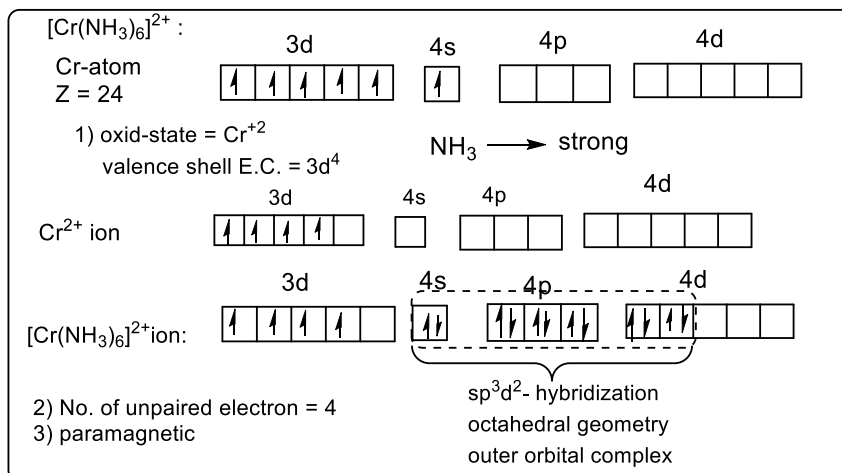
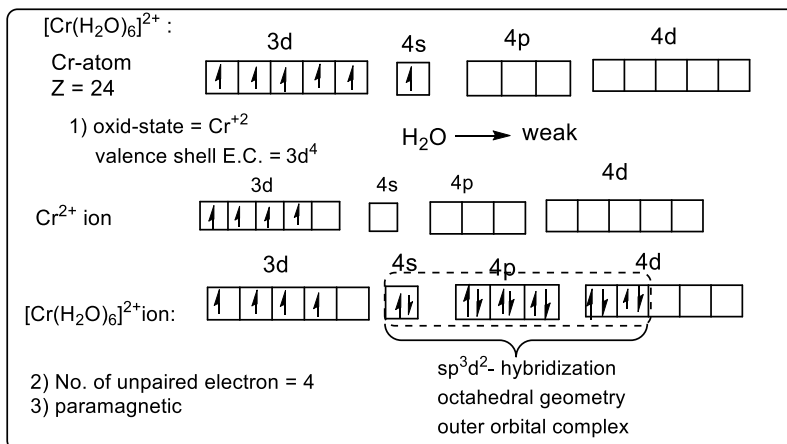
Figure 3.26: Hybridization of $[\text{CoF}_6]^{3-}$

- ii. $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$: This is a very interesting example in which the central metal atom is Fe having the oxidation state as +1. The Fe^+ constitutes to the $3d^6 4s^1$ configuration. The only one nitrosyl (NO^+) ligand as a little tendency to pair the electrons and hence it pairs two electrons that are present in the d orbitals. On the other side, the five water ligands has no any tendency to pair up these electrons. Due to this, no d orbital is vacant and the ligand donates its electrons to one 4s and three 4p, two 4d orbitals to give sp^3d^2 hybridization. *This suggests that, only presence of the strong ligand is not the only criteria to pair up electrons but they should have considerable number for pairing up all the d electrons of the metal.*

Figure 3.27: Hybridization of $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$

Precties Que 1 : Assign the oxidation state of iron in $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$

Precties Que 2. How many electrons are present in the set of d orbital of sodium nitroprusside complex $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$



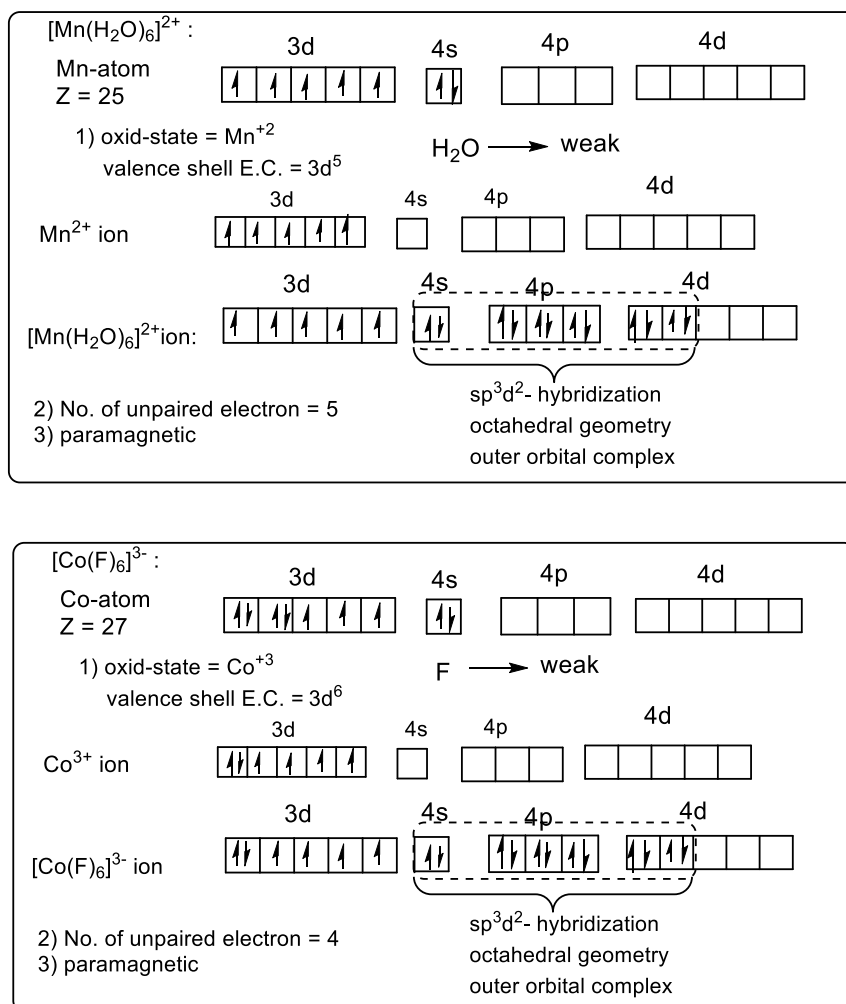


Figure 3.28: Hybridization of some of the outer orbital complexes that shows d²sp³ hybridization

3.2.a. ii. Defects of the Valence Bond Theory

- VBT does not talk about the splitting of the d energy levels of the central cation.
- It is unable to account for the different energy levels of the alternative structures of the complex.
- Electronic spectra and the color properties can't be studied with the help of VBT.
- It doesn't talk about the nature of the ligands i.e. the strong and weak ligands cannot be differentiated with VBT.
- It doesn't explain the reason of pairing of the electrons in case of the strong ligands as it doesn't talk about splitting phenomenon.
- Although it gives the magnetic moment of some of the complexes correctly, it could not explain the temperature dependence of the magnetic properties and the deviation of the calculated moment from the expected one.
- Importantly, this theory doesn't account for the distortion in the geometries of some of the complexes.
- Inorganic reaction mechanism, their rates cannot be studied by this theory.
- It also could not explain why certain complexes are tetrahedral and why some complexes are square planar.
- It could not explain the correct structure of [Cu(NH₃)₄]²⁺
- It also could not explain the peculiarity why certain complexes are inner orbital and why some complexes are outer orbital complexes.

3.2.2. Crystal Field Theory (CFT)

I. Introduction of the crystal field theory: -

The important theories to study the coordination complexes were valence bond theory, crystal field theory, molecular orbital theory and ligand field theory. As we have seen earlier, VBT is useful to visualize bonding in the complexes but there were certain limitations for VBT. Thus to overcome all these limitations, Bethe and van Vleck proposed the crystal field theory. This theory was originally applicable to the ionic crystals and thus the name was given as '*crystal field theory*'.

II. Postulates of the crystal field theory: -

- The central metal ion is surrounded by the ligands that donate at least one lone pair of electrons.
- The ionic ligands such as CN^- , F^- , Cl^- are regarded as the **negative point charges or the simply point charges** and the neutral ligands such as NH_3 , CO are considered as the **point dipoles or simply dipoles**.
- The important assumption is that- there is **no any overlap between the metal orbitals and the ligand orbitals**. There is no any interaction between these orbitals.
- According to this theory, Bonding between the metal and the ligand is not a covalent type. The interaction is considered to be purely electrostatic. Thus the ion-ion interaction is there between the central metal cation and negative ligands. On the other hand, ion- dipole interaction is there between central metal cation and the neutral ligands.
- The d orbitals on the metal have same energy and hence all five d orbitals are said to be **degenerate in the free form**. **However, when the complex is formed, the surrounding ligands remove the degeneracy and the d orbitals, after complex formation, have different energies.**
- The point to be noted is that, in a gaseous state, for an isolated atom of a metal, all the d orbitals are degenerated. If the spherical symmetrical field is applied, the degeneracy is not at all removed and all the d orbitals remain at the same energy. However, the energy of the all the d orbitals is raised because of the repulsion in the field and the electron cloud of the metal.
- In case of the tetrahedral and octahedral complex, the field applied by the ligands is not symmetrical and spherical and d orbitals are not at all affected equally by the ligand field. Thus to understand the crystal field theory, we must know the shapes of the d orbitals:
- As we already know that, there are five d orbitals viz; d_{x^2} and $d_{x^2-y^2}$ atomic orbitals point directly along the axes and d_{xy} , d_{yz} and d_{zx} atomic orbitals point between the axes.
- The point that should be very clear that *all the d orbitals are gerade type*. The reason behind it is opposite lobes have the inversion centre with respect to the wave function. Sometimes inversion centre is also termed as the *centre of inversion or centre of symmetry*.

The shapes of d orbitals in the space are shown as follows: -

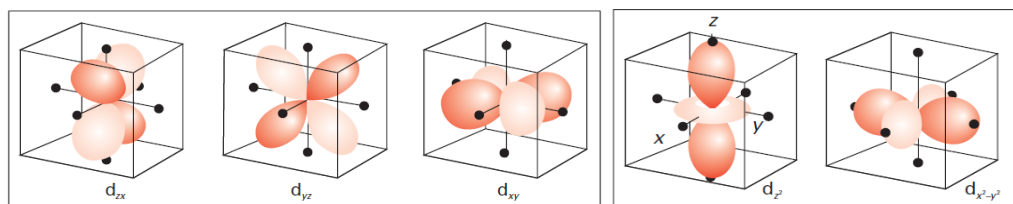


Figure 3.29: shapes of d orbitals in the space

III. Octahedral Complexes:

a) Crystal field splitting in octahedral complexes

- In case of the isolated or free metal cation, all the five d orbitals are degenerated and their energy is same
- In an octahedral complex, let us say $[ML_6]^{n+}$, the metal cation is present at the centre of the regular octahedron and the six ligands that are attached to the metal are placed at the six corners. These all ligands are directed along the Cartesian coordinates i.e. along x, y, and z axes
- If all the six ligands are, let us consider, are at infinite distance from the cation, the metal orbitals will not be affected by the ligand field and hence, in this case, the degeneracy is **not** removed.
- When the ligand starts moving in the direction of the metal cation, the two important forces act that influence the energies of the d orbitals
 - i) Attraction between the electropositive metal and the electronegative ligands
 - ii) Repulsion between the d electrons and the ligand lone pairs
- Greater the force of the ligands, the ligand comes far closer to that of the metal atom, and hence due to this, the repulsion between the metal electrons and the ligand electron increases.
- Also, there is small amount of the repulsion between the ligand and metal orbitals in the space. These two repulsions cause force to adopt the octahedral geometry in which the ligands are situated at the limiting distance.
- All these repulsive forces are responsible for the increase in the potential energy of the total metal-ligand system i.e. complex.
- If the spherical symmetrical field is applied by the ligands in all the directions, the degeneracy is not at all removed and all the d orbitals remain at the same energy. However, the energy of all the d orbitals is raised because of the repulsion in the field and the electron cloud of the metal. *This is a hypothetical concept and has the average energy of a set of d orbitals.*
- ***In case of the octahedral complex, the symmetrical spherical field is never applied, and hence all the d orbitals are not affected to the SAME extent.***
- The two orbitals d_z^2 and $d_{x^2-y^2}$ lie in the direction of the ligand pointing toward and the set of three orbitals d_{xy} , d_{yz} and d_{xz} point between the axes, the orbitals d_z^2 and $d_{x^2-y^2}$ are strongly repelled by the ligand field than the orbitals d_{xy} , d_{yz} and d_{xz} .
- The result of this uneven repulsion is that: the energy of the two orbitals, d_z^2 and $d_{x^2-y^2}$, is raised to the high level and the remaining three energy levels have low energy.
- The point that must be cleared is that, two orbitals, d_z^2 and $d_{x^2-y^2}$ have same energy and are said to be the *doubly degenerated* and referred by the symmetry label e_g , and the three orbitals d_{xy} , d_{yz} and d_{xz} also have same energy but lower than e_g orbitals. The set of d_{xy} , d_{yz} and d_{xz} is called as the t_{2g} which means the *triply degenerate*.
- As in this case, the average metal ligand distance remains same all the time, thus, net potential energy of the system must also remain same as that of the spherical field before splitting. This state of the average is called the *barycenter*.

- The separation of the five d orbitals of metal cation into two sets of orbitals having different energies is called as the **crystal field splitting**. The energy difference is measured in terms of the parameter Δ_o or $10Dq$. The values of the energies is shown in the following diagram: -

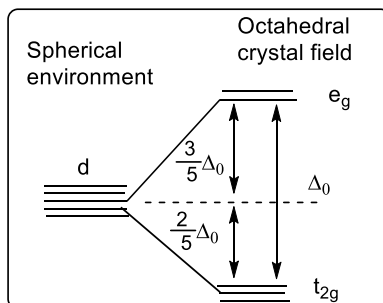


Figure- The energies of the d orbitals in an octahedral crystal field. Note that the Mean energy remains unchanged relative to The energy of the d orbitals in a spherically Symmetrical environment (such as in a free Atom).

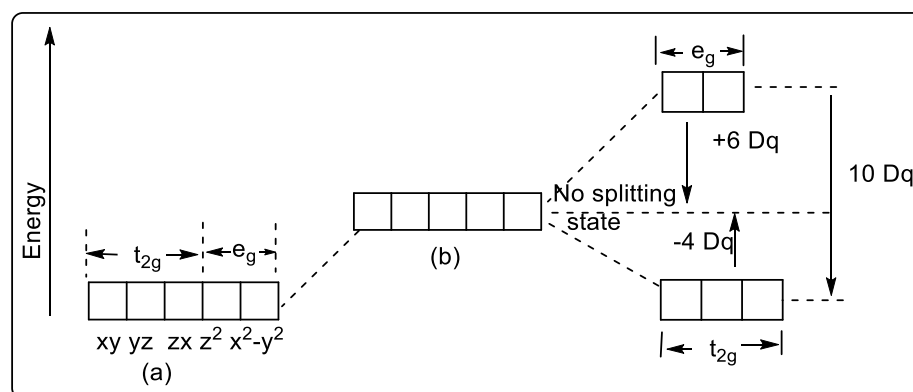
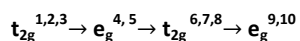


Figure 3.30: Splitting of d orbitals in the octahedral field

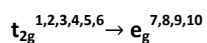
b) Distribution of the electrons in the octahedral complex: -

Distribution of the d electrons in the octahedral complex depends upon the magnitude of the crystal field splitting (Δ_o) and according to the Hund's rule of the maximum multiplicity. If the magnitude of Δ_o is very very small or negligible, then all the d orbitals are said to be degenerated.

Weak field complexes or high spin complexes:- If the magnitude of Δ_o is small, then first three electrons are filled in the t_{2g} orbitals and then the 4th and 5th electron goes to the e_g orbital instead of t_{2g} . Then again the 6th electron comes to the t_{2g} level and hence in this fashion all the electrons are filled. In this case, there is no any pairing takes place of the electrons. Sequence of the filling of the electrons is as follows:



Strong field complexes or low spin complexes: - If the magnitude of Δ_o is large, then first three electrons are filled in the t_{2g} orbitals and then the 4th and 5th electron go to the t_{2g} orbital again instead of e_g . Then the 6th electron comes to the e_g level and hence in this fashion all the electrons are filled. In this case, there is pairing takes place of the electrons. Sequence of the filling of the electrons is as follows:



The complexes having the configuration $d^1, d^2, d^3, d^8, d^9, d^{10}$ cannot be differentiated as high spin or low spin complexes. The electron filling is same in both in case of strong as well as weak filled ligands. Only the complexes of the configuration d^4, d^5, d^6, d^7 are differentiated on the basis of the ligands as high spin or low spin.

It is noted that: **Weak field octahedral complexes are not always the high spin complex.** In case of 3d series, If the oxidation state is greater than 4 and for 4d & 5d series, always form low spin complexes with weak ligands also. e.g. $[\text{NiF}_6]^{2-}$, $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$

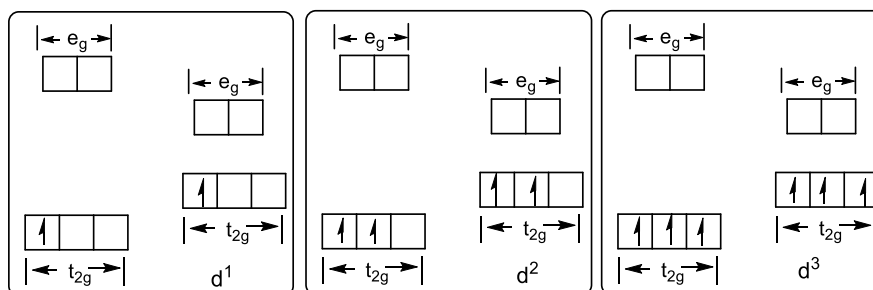
Pairing energy: - The energy to needed to pair up the two electrons is called as the pairing energy. When more than one electron is paired, P becomes the mean pairing energy. Thus, following trend is very important to understand the concept of high spin and the low spin complexes:

Table 3.4: Pairing energy relations with Δ_o

$\Delta_o > P$	Formation of the low spin
$\Delta_o < P$	Formation of the high spin complexes
$\Delta_o = P$	Formation of the low spin complexes and high spin complexes equally
$\Delta_o \gg P$	For 4d and 5d series, always formation of the low spin complex

c) Crystal field stabilization in the octahedral complexes

As we have already discussed that, in case of the octahedral complexes, the degeneracy is removed and the two energy levels such as t_{2g} and e_g are formed. t_{2g} is the lower energy level and e_g is the higher energy level. The separation between the two energy levels is the $10Dq$. The t_{2g} set has energy of $-0.4 \Delta_o$ or $-4 Dq$ and the e_g set has energy of $+0.6 \Delta_o$ or $+6 Dq$ with respect to the barycenter. Negative and positive sign indicates the decrease and increase in the energy with respect to the barycenter. The energies of the different configurations is given in the following manner:



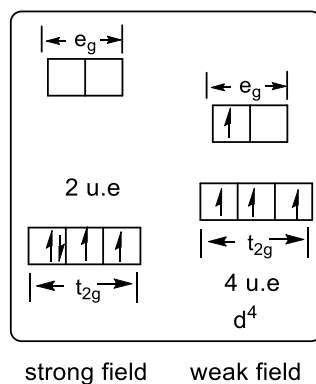
Net energy decrease is called as crystal field stabilization energy (CFSE)

For d^1 , $\text{CFSE} = 1 \rightarrow 0.4 = 0.4 \Delta_o$

For d^2 , $\text{CFSE} = 2 \rightarrow 0.4 = 0.8 \Delta_o$

For d^3 , $\text{CFSE} = 3 \rightarrow 0.4 = 1.2 \Delta_o$

There are two possibilities for metal ions having d^4 - d^7 electronic configuration. Depending on the nature of the ligands and the metal, they could be HIGH SPIN or LOW SPIN complexes. They can be shown as below:



There are two possibilities for metal ions having

d^4 - d^7 electronic configuration.

Depending on the nature of the ligand and the metal they

Could be High spin or Low spin complex.

For the d^4 system CFSE=

For high spin , $(3 \times 0.4) - (1 \times 0.6) = 0.6\Delta_0$

For low spin , $(4 \times 0.4) = 2.6\Delta_0$

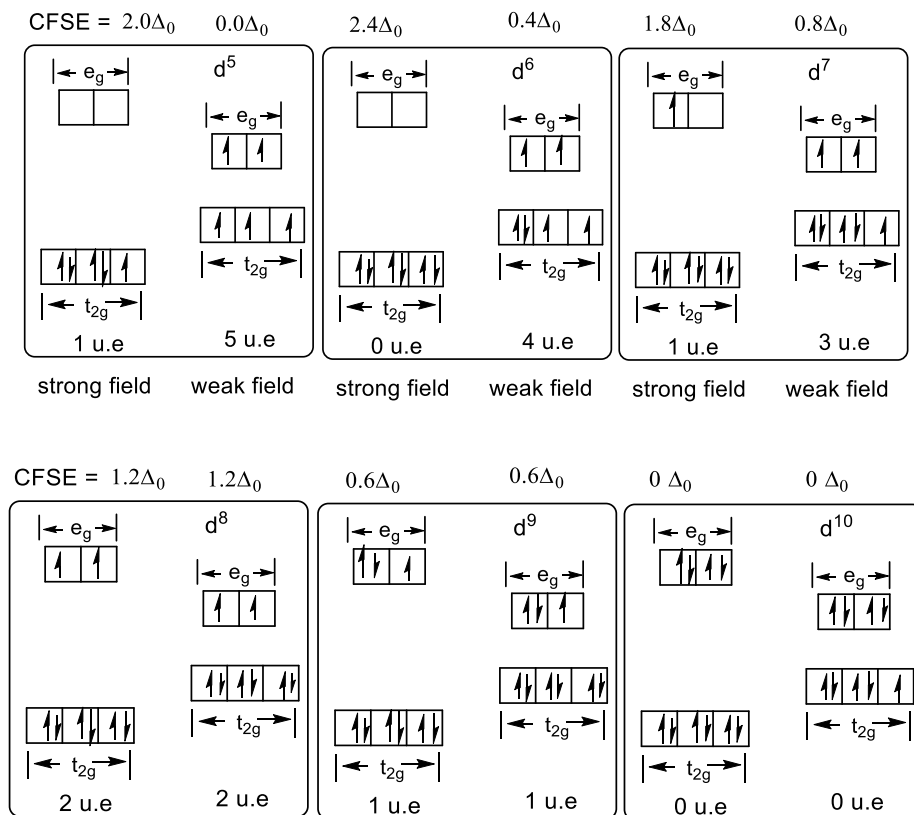


Figure 3.12: Formation of high spin and low spin complexes with their energies

For d^8 , CFSE = $(6 \times 0.4) - (2 \times 0.6) = 1.2\Delta_0$

For d^9 , CFSE = $(6 \times 0.4) - (3 \times 0.6) = 0.6\Delta_0$

For d^{10} , CFSE = $(6 \times 0.4) - (4 \times 0.6) = 0.0\Delta_0$

In all the electronic configurations involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons.

Table 3.5: Distribution of electrons in the octahedral complexes

Configuration		High Spin	Low Spin
d^1	$t_{2g}^1 e_g^0$	$0.4 \Delta_o$	$t_{2g}^1 e_g^0$ $0.4 \Delta_o$
d^2	$t_{2g}^2 e_g^0$	$0.8 \Delta_o$	$t_{2g}^2 e_g^0$ $0.8 \Delta_o$
d^3	$t_{2g}^3 e_g^0$	$1.2 \Delta_o$	$t_{2g}^3 e_g^0$ $1.2 \Delta_o$
d^4	$t_{2g}^3 e_g^1$	$0.6 \Delta_o$	$t_{2g}^4 e_g^0$ $2.6 \Delta_o$
d^5	$t_{2g}^3 e_g^2$	$0.0 \Delta_o$	$t_{2g}^5 e_g^0$ $2.0 \Delta_o$
d^6	$t_{2g}^4 e_g^2$	$0.4 \Delta_o$	$t_{2g}^6 e_g^0$ $2.4 \Delta_o$
d^7	$t_{2g}^5 e_g^2$	$0.8 \Delta_o$	$t_{2g}^6 e_g^1$ $3.2 \Delta_o$
d^8	$t_{2g}^6 e_g^2$	$1.2 \Delta_o$	$t_{2g}^6 e_g^2$ $1.2 \Delta_o$
d^9	$t_{2g}^6 e_g^3$	$0.6 \Delta_o$	$t_{2g}^6 e_g^3$ $0.6 \Delta_o$
d^{10}	$t_{2g}^6 e_g^4$	$0.0 \Delta_o$	$t_{2g}^6 e_g^4$ $0.0 \Delta_o$

IV. Tetrahedral Complexes

a. Crystal field splitting in tetrahedral complexes

- As we already know that, in the Free State, all the d orbitals are degenerated and have the same energy levels.
- In case of the tetrahedral complexes also, the degeneracy is removed because of application of the unsymmetrical field.
- A regular tetrahedral geometry is obtained when a metal cation is situated at the centre and the ligands are situated at the alternate corners of the cube.
- In this tetrahedral arrangement, ligands don't approach directly the metal orbitals instead they come closer to the orbitals directing the corners of the cube edges (d_{xy} , d_{yz} and d_{zx}) than to those who are facing to the corners of the cube faces (d_z^2 and $d_{x^2-y^2}$). Hence the t_2 (*triply degenerated*) orbitals raised in the energy than that of the e orbitals (*doubly degenerated*). The subscript "g" is not written in this case as tetrahedral geometry doesn't possess the centre of inversion.
- The splitting of the tetrahedral field is shown in the following figure: -

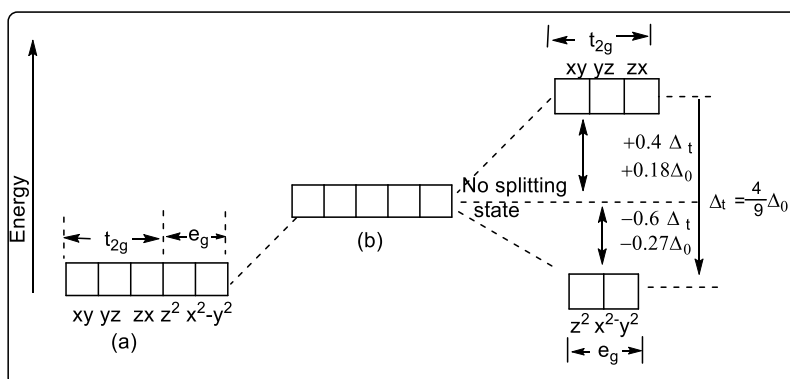


Figure 3.31: Splitting of d orbitals in the tetrahedral field

NOTE: -

- The magnitude of the tetrahedral splitting less than that of the splitting of the octahedral field. There two main reasons for this:
 - i) There are four ligands instead of six ligands, thus field is reduced to the two third values and thus, ligand field value also reduces to the two third values.
 - ii) The direction of the orbitals does not match with the direction of the ligand. This factor also reduces the value by further two third means.

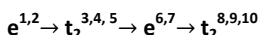
Thus for the same metal ion, the relation can be written as follows: -

$$\Delta_t = \frac{2}{3} \times \frac{2}{3} \times \Delta_o$$

b. Distribution of the electrons in the tetrahedral complex: -

In case of the tetrahedral complexes, the crystal field splitting is low due to earlier mentioned reasons. Thus the electron filling is done according to the Hund's rule of maximum multiplicity. In case of the tetrahedral complexes, e is the lower energy level which is *doubly degenerated* and the t_2 is the higher energy level which is the *triply degenerated*. The first two electrons are filled in the e level which is the low energy level. Due to low splitting, further the electron is filled into the t_2 level instead of getting paired in the e level. And henceforth all the electrons are filled accordingly. The pairing then and only then takes place when each of the five-energy level is singly occupied. For tetrahedral complexes, $\Delta_t < P$

Thus, it can be generalized that- "**All tetrahedral complexes are high spin irrespective of the ligands.**"

**Distribution of electrons in the tetrahedral complexes**

Tetrahedral splitting is seldom large enough to result in the pairing of the electrons. As a result of this, low spin tetrahedral complexes are not very common. A rare example is $[\text{Cr}(\text{NSiMe}_3)_2]_3 [\text{NO}]$.

Table 3.6a: Distribution of electrons in the tetrahedral complexes

	High Spin	
d^1	$e^1 t_2^0$	$0.6 \Delta_o$
d^2	$e^2 t_2^0$	$1.2 \Delta_o$
d^3	$e^2 t_2^1$	$0.8 \Delta_o$
d^4	$e^2 t_2^2$	$0.4 \Delta_o$
d^5	$e^2 t_2^3$	$0.0 \Delta_o$
d^6	$e^3 t_2^3$	$0.6 \Delta_o$
d^7	$e^4 t_2^3$	$1.2 \Delta_o$
d^8	$e^4 t_2^4$	$0.8 \Delta_o$
d^9	$e^4 t_2^5$	$0.4 \Delta_o$
d^{10}	$e^4 t_2^6$	$0.0 \Delta_o$

Table 3.6b: CFSE of Tetrahedral complex

Configuration	High Spin	
d^1	$e^1 t_2^0$	$-0.27 \Delta_o$
d^2	$e^2 t_2^0$	$-0.54 \Delta_o$
d^3	$e^2 t_2^1$	$-0.36 \Delta_o$
d^4	$e^2 t_2^2$	$-0.18 \Delta_o$
d^5	$e^2 t_2^3$	$0.0 \Delta_o$
d^6	$e^3 t_2^3$	$-0.27 \Delta_o$
d^7	$e^4 t_2^3$	$-0.54 \Delta_o$
d^8	$e^4 t_2^4$	$-0.36 \Delta_o$
d^9	$e^4 t_2^5$	$-0.18 \Delta_o$
d^{10}	$e^4 t_2^6$	$0.0 \Delta_o$

c. Crystal field stabilization in the tetrahedral complexes

As we have already discussed that, in case of the tetrahedral complexes, the degeneracy is removed and the two energy levels such as e and t_2 are formed. e is the lower energy level and t_2 is the higher energy level. The separation between the two energy levels is the $10Dq$. The e set has an energy of $-0.6 \Delta_t$ or $-6 Dq$ and the t_2 set has an energy of $+0.4 \Delta_t$ or $+4 Dq$ with respect to the barycenter. Negative and positive sign indicates the decrease and increase in the energy with respect to the barycenter. The energies of the different configurations is given in the following manner:

$$\Delta_{\text{tet}} = \frac{4}{9} \Delta_{\text{oct}} \approx \frac{1}{2} \Delta_{\text{oct}}$$

V. Square planar complexes

a. Distribution of electrons and Crystal field splitting in the square planar complexes

A square planar arrangement of ligands can be formally derived from an octahedral array by removal of two Trans ligands. The metals such as Ni, Pt, Pd forms the square planar complexes in their +2 oxidation states. If we remove the ligands lying along the z axis in the octahedral geometry, then the dz^2 orbital is greatly stabilized; the energies of the dyz and dxz orbitals are also lowered, although to a smaller extent. The resultant ordering of the metal d orbitals is shown at the left-hand side of Figure.

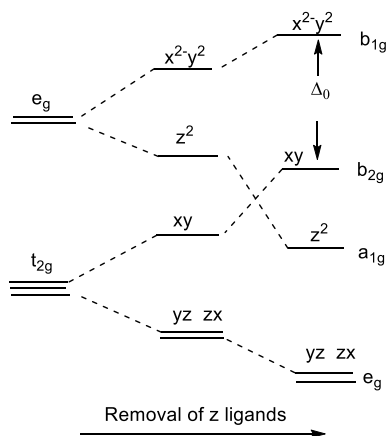


Figure 3.32: Crystal field splitting in the square planar complexes

The fact that square planar d^8 complexes such as $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic is a consequence of the relatively large energy difference between the dx^2-y^2 and $ddxy$. This can be explained on the basis of the $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$. Consider the splitting diagrams shown in figure For $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$, the eight electrons occupy the d orbitals as follows:

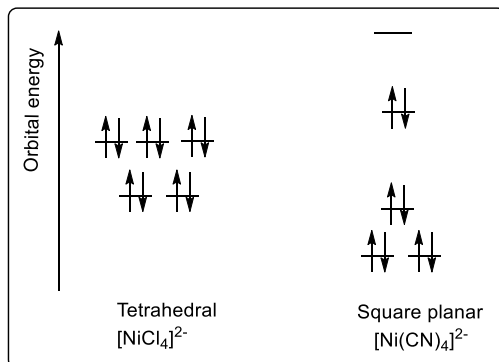


Figure 3.33: Splitting diagrams for $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$

Thus, $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic as it can be seen that, in the tetrahedral case, two unpaired electrons are present. There are no any unpaired electrons present in the square planar case resulting the diamagnetic complex. It is observed that, $\Delta_{sp} = 1.3 \Delta_0$

VI. Different geometries:

a. Crystal field splitting of different geometries: -

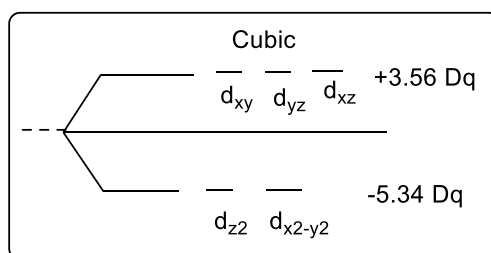


Figure 3.34: Splitting diagram for cubic field

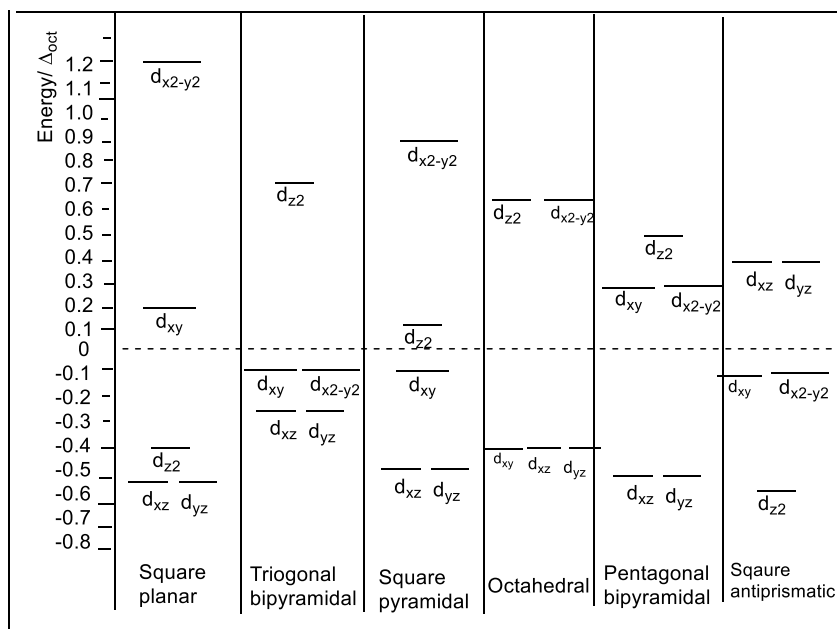


Figure 3.35: Splitting diagram for different types of the fields

The comparative study of the tetrahedral crystal field and the octahedral field is given in the following table:

Table 3.7: Comparative study of the tetrahedral crystal field and the octahedral field

Total d-Electrons	CFSE(Octahedral)		CFSE(Tetrahedral)		OSPE(for high spin complexes)**
	High spin	Low spin	Configuration	Always High spin*	
d^0	$0\Delta_o$	$0\Delta_o$	e^0	$0\Delta_t$	$0\Delta_o$
d^1	$-2/5\Delta_o$	$-2/5\Delta_o$	e^1	$-3/5\Delta_t$	$-6/45\Delta_o$
d^2	$-4/5\Delta_o$	$-4/5\Delta_o$	e^2	$-5/5\Delta_t$	$-12/45\Delta_o$
d^3	$-6/5\Delta_o$	$-6/5\Delta_o$	$e^2 t_2^1$	$-2/5\Delta_t$	$-38/45\Delta_o$
d^4	$-3/5\Delta_o$	$-8/5\Delta_o + P$	$e^2 t_2^2$	$-2/5\Delta_t$	$-19/45\Delta_o$
d^5	$0\Delta_o$	$-10/5\Delta_o + 2P$	$e^2 t_2^3$	$0\Delta_t$	$0\Delta_o$
d^6	$-2/5\Delta_o$	$-12/5\Delta_o + P$	$e^3 t_2^3$	$-3/5\Delta_t$	$-6/45\Delta_o$
d^7	$-4/5\Delta_o$	$-9/5\Delta_o + P$	$e^4 t_2^3$	$-6/5\Delta_t$	$-12/45\Delta_o$
d^8	$-6/5\Delta_o$	$-6/5\Delta_o$	$e^4 t_2^4$	$-4/5\Delta_t$	$-38/45\Delta_o$
d^9	$-3/5\Delta_o$	$-3/5\Delta_o$	$e^4 t_2^5$	$-2/5\Delta_t$	$-19/45\Delta_o$
d^{10}	0	0	$e^4 t_2^6$	$-0\Delta_t$	$0\Delta_o$

VII. Energy difference: Δ

a. Measurement of the Δ_o :-

The distance between the lower energy level and the higher energy level can easily be calculated by recording the UV Visible spectrum of the complexes.

Consider the complex where the central metal have the configuration d^1 e.g. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, as the complex is octahedral, it has t_{2g} level at ground state and e_g level as an excited level. Only electron present is situated at the t_{2g} level. If the radiation of the correct wavelength is absorbed by the complex, the electron is promoted to the highest level and the transition t_{2g} to e_g or $d-d$ transition takes place. According to the UV Visible spectroscopy, the steep curve at 27000 to 30000 cm^{-1} is due to the charge transfer spectra. Importantly, the single transition results in the one band that appears at 20300 cm^{-1}

Since, 1 kJ/mol = 87.3 cm^{-1} , the value of complex at 20300 cm^{-1} comes out to be 243 KJ/mol. this method using the UV Visible spectroscopy for the determination of Δ_o is very much convenient over the years. Also, the value of Δ_o can also be obtained from the lattice energies and the Born Lande equations.

Because the crystal field of d orbitals, the single d electrons in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ occupies an energy level $2/5 \Delta_o$ below the average energy of d orbitals, as a result the complex is more stable. The CFSE in this case is $2/5 \times 243 = 92 \text{ kJ/mol}$.

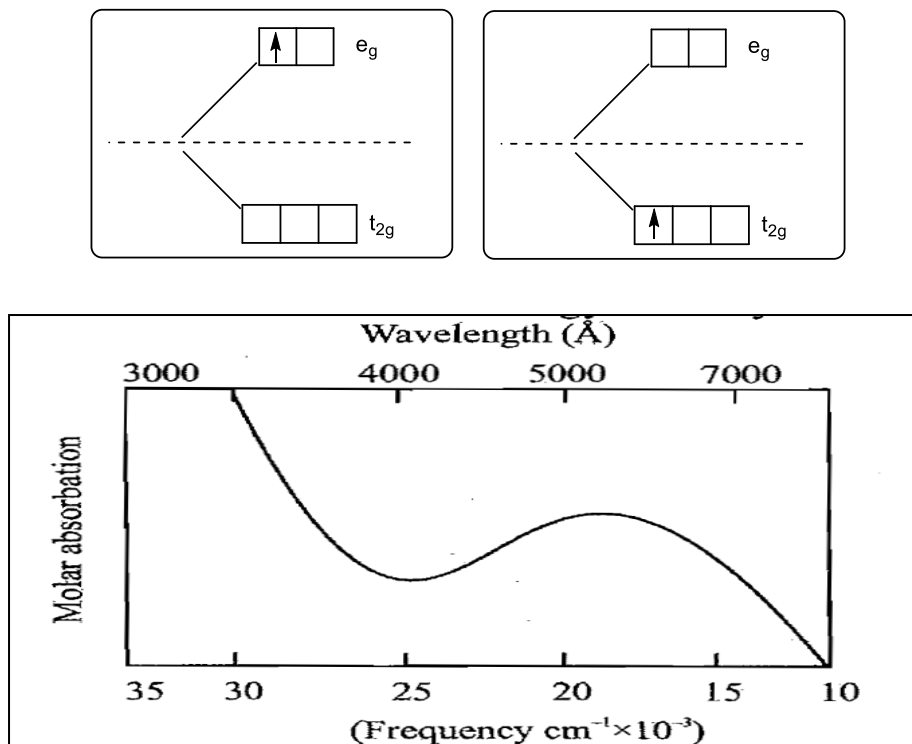


Figure 3.36: Representative diagram for electronic transition

b. Factors affecting the values of the Δ_o :-

i. Nature of the central metal ion: -

- a) Oxidation state of the central metal atom:** If different metal cations having same number of d electrons, **higher the oxidation state, higher will be the value of the Δ_o** . The reason is that, higher oxidation state means high positive charge and hence higher is the attraction of the ligands, ultimately higher is the splitting.

For 3d series, the value of Δ_o for M^{3+} complexes is almost 50% larger than that of values of M^{2+} complexes.

For $[\text{V}(\text{H}_2\text{O})_6]^{2+}$, $\Delta_o = 12400 \text{ cm}^{-1} \rightarrow 3d^3$

For $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $\Delta_o = 17400 \text{ cm}^{-1} \rightarrow 3d^3$

For $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $\Delta_o = 9200 \text{ cm}^{-1} \rightarrow 3d^7$

For $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $\Delta_o = 18200 \text{ cm}^{-1} \rightarrow 3d^6$

Same charge on the cation but the different count of the number of d electrons: In this case, if the same oxidation state is there and d electron count is different, **higher the d electron count, lower will be the value of the Δ_o** . The reason is that, as the d electron count increases, the repulsion increases and ligand can't come closer to the metal and hence the splitting also decreases.

Δ_o decreases with increase in the number of d electrons

For $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $\Delta_o = 9300 \text{ cm}^{-1} \rightarrow 3d^7$

For $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$, $\Delta_o = 8500 \text{ cm}^{-1} \rightarrow 3d^8$

$\Delta_o \propto$ Charge on the cation (Same number of the d electrons)

$\Delta_o \propto 1/d$ electrons (Same oxidation states)

- b) **Principal quantum number:-** The trend is change as the principal quantum number changes. Higher the principal quantum number, higher will be the value of the Δ_o .

Δ_o for 5d > Δ_o for 4d > Δ_o for 3d

For $[\text{Co}(\text{NH}_3)_6]^{3+}$, $\Delta_o = 23000 \text{ cm}^{-1} \rightarrow 3d^6$

For $[\text{Rh}(\text{NH}_3)_6]^{3+}$, $\Delta_o = 34000 \text{ cm}^{-1} \rightarrow 4d^6$

For $[\text{Ir}(\text{NH}_3)_6]^{3+}$, $\Delta_o = 41000 \text{ cm}^{-1} \rightarrow 5d^6$

- c) **Nature of the ligands:-**

Stronger is the ligand, stronger will be the value of the Δ_o and Weaker is the ligand, lower will be the value of the Δ_o . The strength of the ligand is specified by the series called as the *spectrochemical series*.

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- (\text{S-bonded}) < \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{NCO}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{acac}^- (\text{acetylacetonate}) < \text{NCS}^- (\text{N-bonded}) < \text{CH}_3\text{CN} < \text{gly} (\text{glycine}) < \text{py} (\text{pyridine}) < \text{NH}_3 < \text{en} (\text{ethylenediamine}) < \text{bipy} (2,2'\text{-bipyridine}) < \text{phen} (1,10\text{-phenanthroline}) < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

The series is totally based upon the experimental basis. This series both consider the π as well as σ bonding. The pattern of the σ donation is written as:-

halide donors < O donors < N donors < C donors

Thus it is found that crystal field splitting done by strong ligands such as CN^- is almost double that is produced by the weak ligands like halides. This is attributed to the π back donation by the metal orbitals to the ligand empty orbitals. In this way, many N donors and C donors act as " π acceptors" by the formation of π bond(s).

Jorgensen Series or spectrochemical series for the central metal atoms:

Trends in values of Δ_{oct} lead to the conclusion that metal ions can be placed in a spectrochemical series which is independent of ligands:

$\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{V}^{2+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Co}^{3+} < \text{Mn}^{4+} < \text{Mo}^{3+} < \text{Rh}^{3+} < \text{Pd}^{3+} < \text{Pt}^{4+}$

- d. **Number of the ligands:-**

Higher the number of ligands, higher will be the value of the Δ and that is the reason why $\Delta_o \gg \Delta_t$

But this concept has a small twist. Although, square planar complex has lesser number of the ligands, it has more crystal field splitting than that of the octahedral complexes. The reasons behind are as follows:

- These complexes are formed by the metals having the d^8 configuration (3d, 4d, 5d) and stronger ligands such as CO or CN^- . As 4d and 5d series have the highest crystal field splitting, square planar complex has lesser number of the ligands, it has more crystal field splitting than that of the octahedral complexes.

- ii. Also, in square planar complexes, the d_{z^2} orbital containing two electrons is stabilized and $d_{x^2-y^2}$ which is vacant is destabilized.

e. Rule of average environment: -

If different types of ligands are present in the same complex, then the total crystal field splitting depends upon the average strengths of all the ligands. Thus, if L and L' are the two types of the ligands in the same complex $[ML'_3L_3]$, their strength depends upon the average values of splitting of $[ML'_6]$ and $[ML_6]$.

$$\text{For } [ML_3L'_3] \text{ complex, } \Delta_0 = \frac{1}{2}\{\Delta_0[ML_6] + \Delta_0[ML'_6]\}$$

$$\text{For } [ML_4L'_2] \text{ complex, } \Delta_0 = \frac{1}{3}\{2\Delta_0[ML_6] + \Delta_0[ML'_6]\}$$

VIII. Tetragonal Distortion Or Jahn Teller Distortion

- As in the octahedral geometry, if all the bond lengths are same, then the geometry is called as the regular octahedral geometry. The regular octahedral geometry arises due to the fact that, the field is symmetric and the ligand exerts the same field strength in all the possible directions. Also, if both the energy levels are symmetrically filled, then the regular octahedral geometry is observed.
- But if there is a case when one of the energy levels, either t_{2g} or e_g are asymmetrically filled, then there is some sort of *distortion* in the regular geometry as the regular octahedral geometry is not at all stable in this case.
- In case of the e_g orbitals which lie along the direction of the ligands, the ligands are repelled more than the others and thus in this case the distortion is very much higher. For the t_{2g} orbitals, that lie in between the ligands, this effective repulsion is less as compared to the previous one and hence a little distortion is there.
- Thus the distortion in the octahedral complexes is called as the *tetragonal distortion*. This type of the distortion occurs when the trans ligands lying at the z axis move away or toward the central metal ion. The away movement of the ligand that increases the bond length results into the elongation and termed as the *tetragonal elongation or z_{out}* . The towards movement of the ligand that decreases the bond length results into the compression and termed as the *tetragonal compression or z_{in}* .

Generalized statement can be written as:

“Any nonlinear molecule in an electronically degenerate state is unstable and the molecule becomes distorted in such a way to remove the degeneracy and lower the symmetry and the energy”

Octahedral complexes of d^9 and high-spin d^4 ions are often distorted, e.g. CuF_2 (the solid state structure of which contains octahedrally sited Cu^{2+} centres) and $[Cr(H_2O)_6]^{2+}$, so that two metal–ligand bonds (axial) are different lengths from the remaining four (equatorial). This is shown in structures (elongated octahedron) and (compressed octahedron).

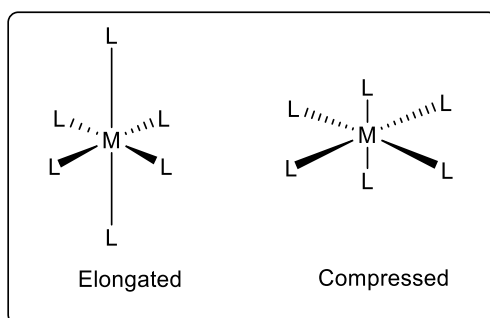


Figure 3.37: Elongation and compression in case of Jahn Teller distortion

For a high-spin d^4 ion, one of the e_g orbitals contains one electron while the other is vacant.

If the singly occupied orbital is in the d_{z^2} , most of the electron density in this orbital will be concentrated between the cation and the two ligands on the z axis. Thus, there will be greater electrostatic repulsion associated with these ligands than with the other four and the complex suffers elongation. In this case the distance between the metal and ligand lying at the z axis increases and thus this is called as the **z-out case**. The energy of d_{z^2} is less than that of the $d_{x^2-y^2}$ and d_{xy} orbitals are more stable. Conversely, If the singly occupied orbital is in the $d_{x^2-y^2}$, most of the electron density in this orbital will be concentrated between the cation and the two ligands on the x and y axis. Thus, there will be lesser electrostatic repulsion associated with these ligands than with the other four and the complex suffers compression. In this case the distance between the metal and ligand lying at the z axis decreases and thus this is called as the **z-in case**. The energy of d_{z^2} is far more than that of the $d_{x^2-y^2}$ and d_{xy} orbitals are more stable.

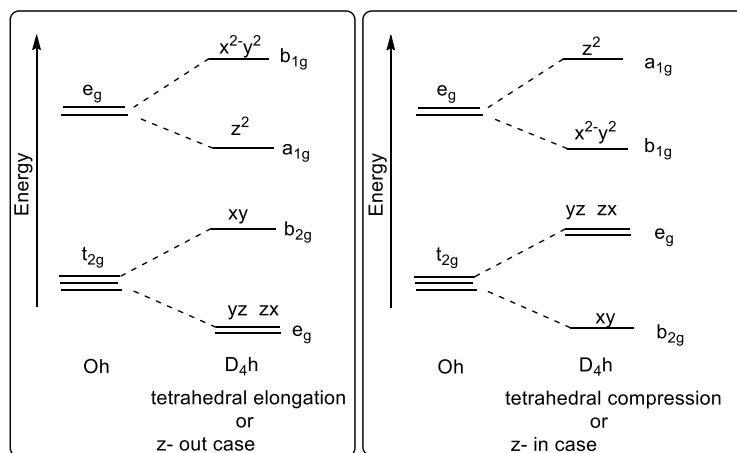


Figure 3.38: [Splitting for Zout and Zin case]

i. Some general facts about the Jahn Teller distortion: -

- If the t_{2g} orbital is asymmetrically filled, the small distortion takes place and this distortion is called as **dynamic distortion or weak distortion**. On the other hand, the e_g orbitals are asymmetrically filled, the distortion takes place and this distortion is called as **strong or non-dynamic distortion**. If both the orbitals are symmetrically filled, then there is no distortion at all.
- The significant distortions were observed in the high spin d^4 , low spin d^7 and d^9 cases. In all these types the e_g are asymmetrically filled containing one, one and three electron(s) respectively.

e.g. high spin d^4 CrF_2 , MnF_3

low spin d^7 NaNiO_2

d^9 CuCl_2 , CuBr_2

- Following diagram will explain the distortion cases for different type of the configurations

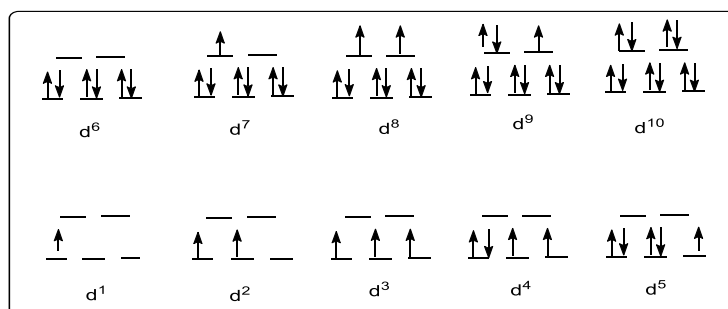


Figure 3.39: Electronic configuration in case of low spin octahedral complexes and J-T distortion

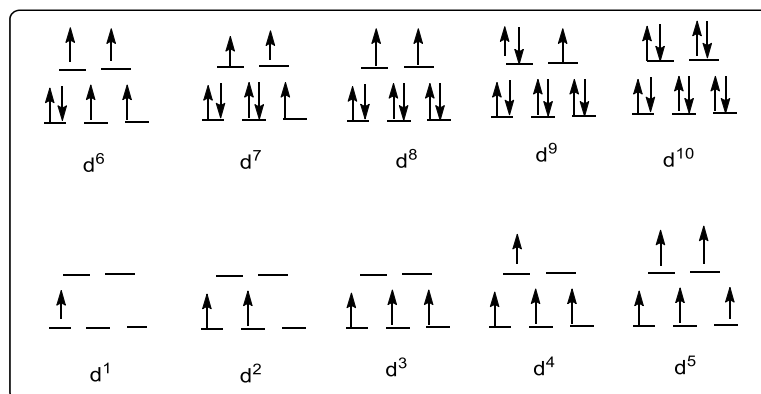


Figure 3.40: Electronic configuration in case of high spin octahedral complexes and J T distortion

- In Ni(II) complex containing four strong and two weak ligands, the distortion happens but not due to Jahn Teller distortion. This distortion is due to the asymmetric field strength applied by different ligands having varying strength.
- In the tetrahedral complexes, d^3, d^4, d^8, d^9 cases show the Jahn Teller distortion. d^3 and d^8 show elongation and d^4 and d^9 show the flattening of the tetrahedral system.

Electronic configuration	t_{2g}	e_g	Nature of ligand field	examples
d^0			strong or weak	$Ti^{IV}O_2$, $[Ti^{IV}F_6]^{2-}$ $[Ti^{IV}Cl_6]^{2-}$
d^3			Strong or weak	$[Cr^{III}(oxalate)_3]^{3-}$ $[Cr^{III}(H_2O)_6]^{3+}$
d^6			Weak	$[Mn^{II}F_6]^{4-}$ $[Fe^{III}F_6]^{3-}$
d^6			Strong	$[Fe^{II}(CN)_6]^{4-}$ $[Co^{III}(NH_3)_6]^{3+}$
d^8			Weak	$[Ni^{II}F_6]^{4-}$ $[Ni^{II}(H_2O)_6]^{2+}$
d^{10}			Strong or weak	$[Zn^{II}(NH_3)_6]^{2+}$ $[Zn^{II}(H_2O)_6]^{2+}$

Figure 3.41: Some examples of high spin and low spin complexes

- There are some complexes in which the Jahn Teller distortion is temperature dependent. The distortion cannot be detected at the room temperature. These distortions are detected at the low temperature or freezing temperature. e.g. octahedral aqua complex of the Ti^{3+} , octahedral aqua complexes of Fe^{2+}

ii. Consequences of the Jahn Teller Distortion: -

Stability of the Cu^{2+} complexes:

- The stability of the complexes of the divalent cations can be illustrated by the Irving – William series. **$\text{Ba(II)} < \text{Sr(II)} < \text{Ca(II)} < \text{Mg(II)} < \text{Mn(II)} < \text{Fe(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$** .
- The extra stability of the Cu is due to the Jahn Teller distortion. During the distortion, two electrons are lowered in the energy while only one is raised by an equal amount of energy.
- Some of the chelating complexes are unstable due to the Jahn Teller distortion due to distortion causes some strain in the complexes. In the following case, cis isomer is less stable than trans partner.
- In crystalline KCuF_3 , two Cu- F distances are less than the four others. This is due to Jahn Teller compression.
- Jahn Teller distortion affects the absorption spectrum. There appears a small nudge in the spectrum due to these distortions.

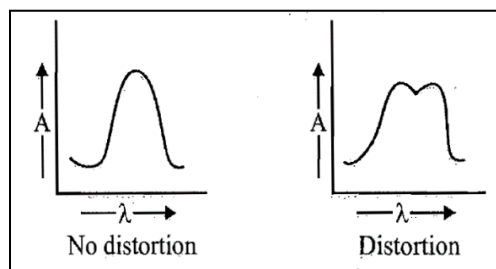
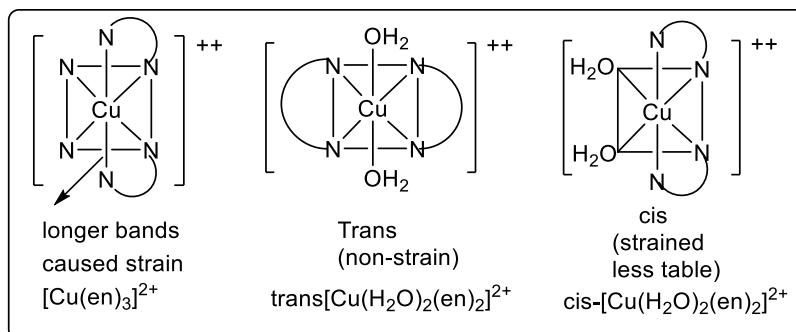


Figure 3.42: Effect of Jahn Teller distortion on the electronic spectrum

- The uneven stability of the Au(II) can be explained on the basis of the Jahn Teller distortion. Some of the complexes of Au(II) are unstable and disproportionate to the Au(I) and Au(III) . On the other hand, Cu(II) and Ag(II) complexes are far more stable due to these distortions. It is expected that the Au(II) must have same stability as that of the Cu(II) and Ag(II) . But the large CFSE makes the system too unstable and the Au(II) undergoes oxidation or reduction to get stability.



IX. Applications of the Crystal Field Theory

Crystal field theory can bring together structures, magnetic properties and electronic properties. Trends in CFSEs provide some understanding of thermodynamic and kinetic aspects of d-block metal complexes. Crystal field theory is surprisingly useful when one considers its simplicity. However, it has limitations. Let us discuss the applications first:

Color and the electronic spectra of the complexes: - The CFT is very important for the interpretation of the color and the spectral properties of the coordination complexes. These all be discussed in the following and upcoming sessions.

Magnetic properties of the complexes: - The CFT is very important for the calculation of the magnetic moments of the complexes. These all be discussed in the following and upcoming sessions.

Enthalpy of hydration of the transition metal ions: - In the aqueous solutions, the metal atom is surrounded by the water molecule and this process is called as the hydration. Hydration energy is the energy released when the gaseous atom gets hydrated.

There are two factors that influences the hydration energy very much:

- Effective nuclear charge – Hydration energy increases as Z_{eff} increases and
- Ionic radius – Hydration energy decreases as the ionic radius increases.

As the nuclear charge increases, the affinity of the water molecule increases and hence the hydration energy also increases. Similarly, across the period, for divalent cations, ionic radius decreases, thus we expect the regular trend in the attraction and ultimately the hydration energy. But the deviations are seen from ideal ones (dotted line) which are concluded on the basis of the experimental studies, because of the evolution of the crystal field stabilization energy.

Thus following relation is confirmed as:

$$\text{Experimental hydration energy} = \text{Theoretical hydration energy} + \text{CFSE}$$

The two humps in the diagram are due to the addition or contribution of the CFSE to the expected hydration energy. Since the hydration energy of Ca, Mn and Zn in +2 oxidation state is zero, these values lie on the straight line and there is no any deviation is observed in this case.

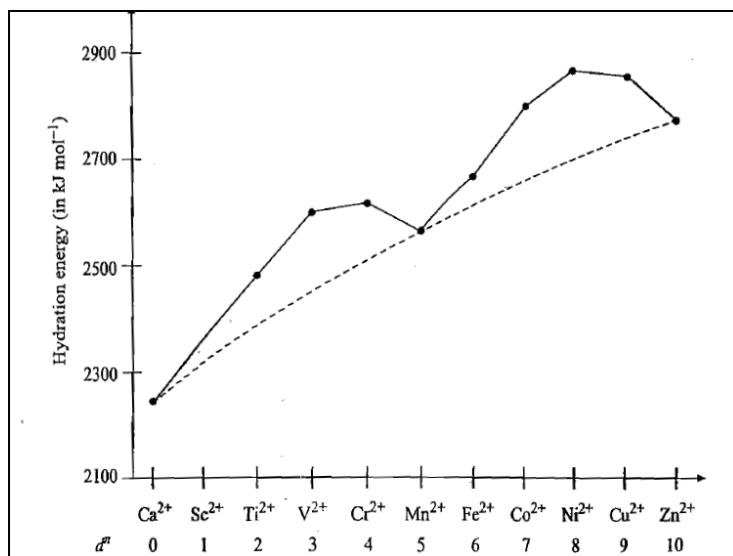
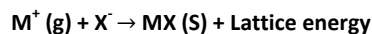


Figure 3.43: Hydration energies of divalent cations

Lattice energy: - Lattice energy is the energy change that is occurred when one mole of the crystal is formed from the gaseous atom. The equation can be written as



Form Born Lande equation:

$$\text{Lattice energy (U)} = -\frac{N_0 A Z^+ Z^-}{r_0} \left(1 - \frac{1}{n}\right)$$

Where, Z = Charge on the ligand

e = charge on an electron

a = distance between metal and ligand

r = distance of an electron from the nucleus

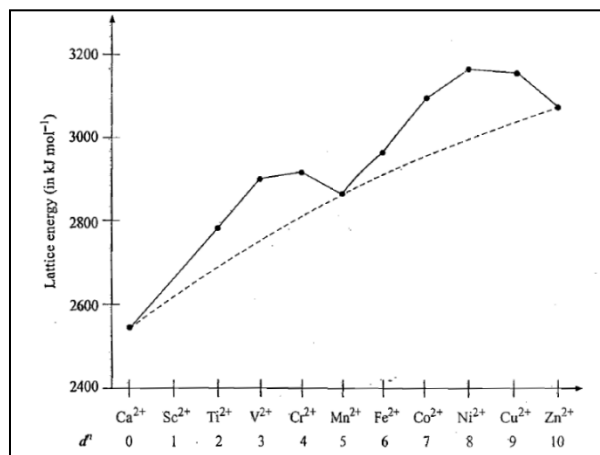


Figure 3.44: Hydration energies of divalent cations

From the above equation, it is observed that the Lattice energy is directly proportional to the charges on the cation and anion that are forming the crystals. It is also inversely proportional to the inter ionic distance. Similar to that of hydration energy, there are some deviations observed from the expected ones. Some metals have higher lattice energies than the expected ones. As the CFSE for different metal cation is different, the deviation which is obtained by the addition of CFSE is also irregular. If the lattice energies of CaCl_2 to ZnCl_2 are plotted as the function of the atomic number, following graphical observations are observed. In this case also, a double humped curve is obtained.

Ionic radius of divalent cations of the 3d series:

The ionic radius of the divalent and trivalent cations of the 3d series are expected to decrease because of increment in the effective nuclear charge and the poor shielding effect of the inner d electrons. Due to this, the attraction between the ligand and metal also expected to increase. But there are some deviations from this fact also. The decrease in the ionic radius in both high spin and low spin case is shown in the following cases:

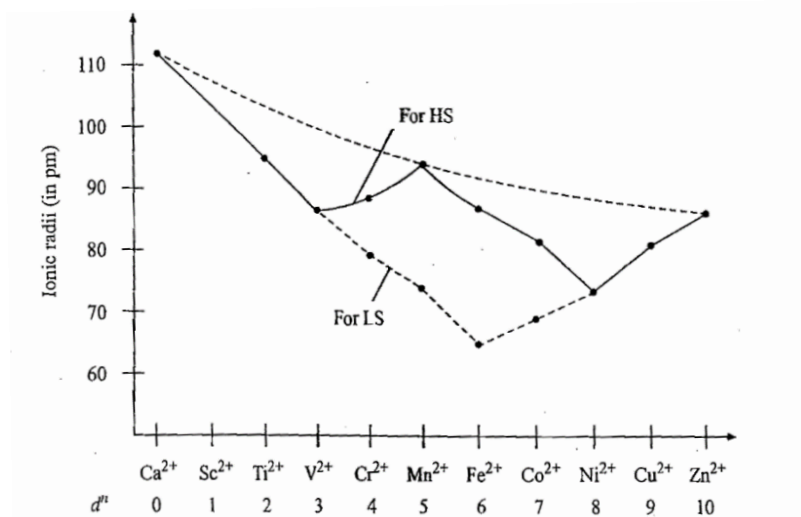


Figure 3.45: Ionic radius of divalent cations

Spinel structure determination:

- Spinel is the mixed metal oxides having the formula AB_2O_4 or $AO.B_2O_3$.
- In this case, A has the charge (II) and B has the formal charge (III). A and B can be group 13 element or the transition element.
- The oxide forms cubic closed packing (ccp) or face centered packing (fcc) with eight tetrahedral voids and four octahedral voids per unit. $1/3^{rd}$ of the metals occupy the tetrahedral voids and $2/3^{rd}$ metal occupy the octahedral voids. *Tetrahedral voids are double than octahedral voids while the octahedral voids are equal to the lattice points.*
- Therefore, the relation is given as:
Number of tetrahedral voids = 2 → number of octahedral voids
Number of octahedral voids = 2 → number of octahedral voids
Number of tetrahedral voids = 2 → number of octahedral voids = 2 → number of lattice points

Ideally there are two types of the spinels:

- Normal spinels** :- In the normal spinels, A^{2+} ions occupy the one eighth of the tetrahedral voids and B^{3+} occupies half of the octahedral voids. General formula of these type is $[A][B_2][O_4]$.
e.g. $MgCr_2O_4$, $MgAl_2O_4$, $NiCr_2O_4$
- Inverse spinels** :- In the inverse spinels, half of the B^{3+} ions have exchanged places with all the A^{2+} ions. In other words, A^{2+} ions occupy $1/4^{th}$ of the octahedral voids along with the half B^{3+} ions whereas other half B^{3+} ions occupy $1/8^{th}$ of the tetrahedral voids. They can be represented by $[A(II) B(III)][B(III)][O_4]$.
e.g. $CrFe_2O_4$, Fe_3O_4 , $NiAl_2O_4$

Prediction of the structure of spinels:

An important factor in the determination of the inverse and the normal spinel is the CFSE of the cations occupying the tetrahedral and octahedral voids. The metal cations in tetrahedral and octahedral voids are thus surrounded by four and six oxide ions respectively. Thus, the metal cations occupying the tetrahedral and octahedral voids are considered to form the tetrahedral and octahedral complexes respectively. **The oxide ion behaves as weak ligands.** Thus, to determine whether the complex is inverse or normal one, we have to compare with the CFSE in tetrahedral and octahedral environment for the ions A^{2+} and B^{3+} .

If CFSE for B^{3+} ion in octahedral voids is greater than that of B^{3+} ion in the tetrahedral and A^{2+} in both tetrahedral and octahedral voids, the spinel will be termed as **normal spinel**.

If CFSE for B^{3+} ion in tetrahedral voids is greater than that of B^{3+} ion in the octahedral voids and A^{2+} in octahedral voids, the spinel will be termed as **inverse spinel**.

i. $Mn_3O_4 \rightarrow Mn(II)Mn_2(III)O_4$

O^{2-} behaves as a weak ligand.

Octahedral	Tetrahedral
$Mn^{2+}(d^5)t_{2g}^3 e_g^2$	$e^2 t_2^3$
CFSE = $[-0.4 \times 3 + 0.6 \times 2]\Delta_0$	CFSE = $[-0.27 \times 2 + 0.18 \times 3]\Delta_0$
= 0	= 0
$Mn^{3+}(d^4)t_{2g}^3 e_g^1$	$e^2 t_2^2$
CFSE = $[-0.4 \times 3 + 0.6 \times 1]\Delta_0$	CFSE = $[-0.27 \times 2 + 0.18 \times 2]\Delta_0$
= $-0.6 \Delta_0$	= $-0.18 \Delta_0$

Therefore, it is observed that the CFSE for Mn^{3+} ion is greater in the octahedral field; thus it is stable in the octahedral environment. Thus Mn^{3+} occupies the octahedral voids and Mn^{2+} occupy the tetrahedral voids. Thus, it is a *normal spinel*.

ii. $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe(II)Fe}_2\text{(III)O}_4$

Octahedral	Tetrahedral
$\text{Fe}^{2+}(\text{d}^6)t_{2g}^4 e_g^2$	$\text{e}^3 t_2^3$
$\text{CFSE} = [-0.4 \times 4 + 0.6 \times 2]\Delta_0$	$\text{CFSE} = [-0.27 \times 3 + 0.18 \times 3]\Delta_0$
$= -0.4 \Delta_0$	$= -0.27 \Delta_0$
$\text{Fe}^{3+}(\text{d}^5)t_{2g}^3 e_g^2$	$\text{e}^2 t_2^3$
$\text{CFSE} = [-0.4 \times 3 + 0.6 \times 2]\Delta_0$	$\text{CFSE} = [-0.27 \times 2 + 0.18 \times 3]\Delta_0$
$= 0$	$= 0$
Since CFSE for Fe^{2+} in octahedral field is highest.	

Therefore, it is observed that the CFSE for Fe^{2+} ion is greater in the octahedral field; thus, it is stable in the octahedral environment. Thus Fe^{2+} occupies the octahedral voids and Fe^{3+} occupies the tetrahedral voids. Thus, it is an *inverse spinel*.

There is a simple trick for the determination of the inverse spinel and normal spinel using the parameter lambda (λ) also called as occupation factor. If $\lambda = 0$ then, it is a normal spinel and $\lambda =$ more than zero to 0.50, then it is an inverse spinels.

Table 3.8: Determination of the inverse spinel and normal spinel using the parameter lambda (λ)

$\text{B}^{3+}/\text{A}^{2+}$	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Al^{3+}	0	0	0	0	0.38	-	0
Cr^{3+}	0	0	0	0	0	0	0
Fe^{3+}	0.45	0.1	0.50	0.50	0.50	0.50	0
Mn^{3+}	-	0	-	-	-	-	0
Co^{3+}	-	-	-	0	-	-	0

Although, crystal field theory quite successfully rationalizes observed structures of the spinels of the first transition series, it must be applied with carefully to the other examples. In comparing structures in which other factors like ionic radii, covalence and etc. are more dissimilar, d orbitals splitting along generally don't explain the observation. In these cases, a broader analysis is required.

X. Merits of the Crystal Field Theory

- CFT successfully explains the structure of the complex along with the geometries and the bonding.
- Magnetic properties of the complexes are explained on the basis of CFT.
- Color properties of the complexes can be determined by the CFT.
- Thermodynamic and the kinetic aspects are illustrated by using CFT which are far more important for reaction mechanism.
- Spinel structure can be found out and hence the type of cation.
- Hydration energies and the lattice energies can be calculated

XI. Demerits of the Crystal Field Theory

- CFT considers only metal d orbitals and s and p orbitals are ignored in each and every study.
- Covalent character cannot be explained on the basis of CFT.
- Importantly, π bonding is ignored in the CFT.
- CFT does not explain about the ligand strength in the spectrochemical series.
- The compounds like $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$ in which the metal is in the zero oxidation state and the ligand is neutral have no electrostatic attraction between metal and ligands.

Chapter 4

Term Symbol and Electronic Spectra of the Coordination Compounds

4.1. Term Symbols

4.1.1. Microstates: -

The electronic configuration of an atom, ion or molecule is not the complete description of arrangement of the electrons in a subshell of an atom. In the configuration p^2 , for instance, the two electrons might occupy orbitals with different orientations of their orbital angular momentum (i.e., with different values of m_l from among the possibilities +1, 0, -1 that are available when $l = 1$). Similarly, the designation p^2 tells us nothing about the spin orientations of the two electrons $m_s +\frac{1}{2}$ or $-\frac{1}{2}$. The atom may in fact have several different states of total orbital and spin angular momentum, each one corresponding the occupation of orbital with different values of m_l by electrons with different values of M_s . The different ways in which the electrons can occupy the orbitals specified in the configuration are called *microstates of the configuration*.

Following formula is useful to calculate the number of microstates of the given configuration; -

$$\text{No. of microstates} = \frac{N!}{x!(N-x)!}$$

$$N = 2(2l + 1) = \text{Twice the no. of orbitals}$$

x = Number of electrons.

For p^2 configuration,

$$p^2, N = 6, x = 2$$

$$\text{No. of microstates} = \frac{6!}{2!(6-2)!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 \times 4 \times 3 \times 2 \times 1} = 15$$

That means, the two electrons can be arranged in the three p orbitals in 15 different ways without having the two electrons all four-quantum number same.

4.1.2 The number of microstates

The number of microstates of a system corresponds to the total number of distinct arrangements for e^- number of electrons to be placed in number of possible orbital positions. Given some electron configuration, the following formula can be used to determine the number of microstates:

$$\text{Number of microstates} = \frac{(\text{Total number of electrons that orbital can accommodate})!}{(\text{Actual number of electrons})! \times (\text{Total electrons} - \text{actual electrons})!}$$

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! \times (N-n)!}$$

This can be explained using some examples of the actual configurations:

1. s^1 configuration:

We know that, s orbital accommodates total 2 electrons hence the value of N is 2.

Given that, s orbital actually contains 1 electron, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! \times (N-n)!} = \frac{2!}{(1)! \times (2-1)!} = 2$$

Thus, this 1 electron can be arranged in 2 different ways in which at least one quantum number of that electron is different.

2. s^2 configuration:

We know that, s orbital accommodates total 2 electrons hence the value of N is 2.

Given that, s orbital actually contains 2 electrons, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! \times (N-n)!} = \frac{2!}{(2)! \times (2-2)!} = 1$$

Thus, these 2 electrons can be arranged in only 1 different way in which at least one quantum number of that electrons is different.

3. p^1 configuration:

We know that, p orbital accommodates total 6 electrons hence the value of N is 6.

Given that, p orbital actually contains 1 electron, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! \times (N-n)!} = \frac{6!}{(1)! \times (6-1)!} = 6$$

Thus, this 1 electron can be arranged in 6 different ways in which at least one quantum number of that electron is different.

4. p^2 configuration:

We know that, p orbital accommodates total 6 electrons hence the value of N is 6.

Given that, p orbital actually contains 2 electrons, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! \times (N-n)!} = \frac{6!}{(2)! \times (6-2)!} = 15$$

Thus, these 2 electrons can be arranged in 15 different ways in which at least one quantum number of that electrons is different.

5. p^3 configuration:

We know that, p orbital accommodates total 6 electrons hence the value of N is 6.

Given that, p orbital actually contains 3 electrons, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! X (N-n)!} = \frac{6!}{(3)! X (6-3)!} = 20$$

Thus, these 3 electrons can be arranged in 20 different ways in which at least one quantum number of that electrons is different.

Hole Formalism:

Now, at this point, it is very essential to mention the concept of hole formalism.

It states that for many electronic properties one may consider systems with e or (N-n), the number of unoccupied sites or "holes", to be equivalent.

Thus, p^4 configuration = $p^{(6-2)} = p^2$ configuration

p^5 configuration = $p^{(6-1)} = p^1$ configuration

The same is true for all p, d, f, ... systems such as d^1/d^9 or f^2/f^{12} and so on.

6. d^1 configuration:

We know that, d orbital accommodates total 10 electrons hence the value of N is 10.

Given that, d orbital actually contains 1 electron, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! X (N-n)!} = \frac{10!}{(1)! X (10-1)!} = 10$$

Thus, this 1 electron can be arranged in 10 different ways in which at least one quantum number of that electrons is different.

7. d^2 configuration:

We know that, d orbital accommodates total 10 electrons hence the value of N is 10.

Given that, d orbital actually contains 2 electrons, hence by applying the formula, we get,

$$\therefore \text{Number of microstates} = \frac{N!}{(n)! X (N-n)!} = \frac{10!}{(2)! X (10-2)!} = 45$$

Thus, these 2 electrons can be arranged in 45 different ways in which at least one quantum number of that electrons is different.

Hence, same method and law of Hole formalism can be used to calculate for the remaining of d and f configurations.

If one should consider an atom with multiple unoccupied orbitals, the total number of microstates will equal the product of the microstates for the individual orbitals.

For an $s^1 p^2$ configuration, the total number of microstates will equal the product of the microstates for these individual orbitals.

Thus, microstates of an $s^1 p^2$ configuration, microstates = 2 (from S^1) X 15 (from p^2) = 30.

The possible arrangement, total M_L , M_S and M_J values are also shown in the following table:

Table 4.1: Possible arrangement, total M_L , M_S and M_J values

$m_l = +1$	$m_l = 0$	$m_l = -1$	M_L	M_S	M_J
$\uparrow\downarrow$			2	0	2
	$\uparrow\downarrow$		0	0	0
		$\uparrow\downarrow$	-2	0	-2
\uparrow	\uparrow		1	1	2
\uparrow		\uparrow	0	1	1
	\uparrow	\uparrow	-1	1	0
\downarrow	\downarrow		1	-1	0
\downarrow		\downarrow	0	-1	-1
	\downarrow	\downarrow	-1	-1	-2
\uparrow	\downarrow		1	0	1
\downarrow	\uparrow		1	0	1
\uparrow		\downarrow	0	0	0
\downarrow		\uparrow	0	0	0
	\uparrow	\downarrow	-1	0	-1
	\downarrow	\uparrow	-1	0	-1

4.1.2. Spectroscopic Terms: -

The microstates of a given configuration have the same energy only if inter electronic repulsions are negligible. However, because atoms and most molecules are compact, inter electronic repulsions are strong and cannot always be ignored. As a result, microstates that correspond to different relative spatial distributions of electrons have different energies. If we group together the microstates that have the same energy when electron repulsions are taken into account, we obtain the spectroscopically distinguishable energy levels called **Terms**.

The values of L correspond to **atomic states** described as S, P, D, Fin a manner similar to the designation of atomic orbitals s, p, d, f

Following table shows the values of L that corresponds to the different atomic states.

Table 4.2: L that corresponds to the different atomic states

L value	0	1	2	3	4	5	6
Atomic State	S	P	D	F	G	H	I

It is to be noted that, the values of S are used to calculate the spin multiplicity $2S + 1$. Finally, the term is obtained by writing spin multiplicity as superscript to the state.

$$\text{Term} = {}^{2S+1}L$$

The state having multiplicity of 1, 2, 3 or 4 are described as singlet, doublet, triplet or quartet states respectively.

Table 4.3: Relation between number of unpaired electrons and the spin multiplicity: -

Number of unpaired electrons	S	Spin multiplicity (2s+1)	State
0	0	1	Singlet
1	1/2	2	Doublet
2	1	3	Triplet
3	3/2	4	Quartet
4	2	5	Quintet
5	5/2	6	Sextet

4.1.3. Term Symbols:

If we know $(2S + 1)$, L and J for an energy state, we can write the full-term symbol. This is done by writing the symbol of the value of L (i.e. S, P, D . . .) with the value of $(2S + 1)$ as a left-superscript and the value of J as a right subscript. The term symbol for the particular state is written as follows-

$$\text{Term symbol} = {}^{2S+1}L_J$$

Where the numerical superscript gives the multiplicity of state, the numerical subscript gives the total angular momentum quantum number J and the value of orbital quantum no. L is expressed by a letter.

For $L = 0, 1, 2, 3, 4, \dots$ symbol are S, P, D, F, G respectively.

Thus, for example, the electronic ground state of carbon is 3P_0 ('triplet P zero') denoting $L = 1$, $(2S + 1) = 3$ (i.e. $S = 1$) and $J = 0$. Different values of J denote different levels within the term, i.e. ${}^{(2S+1)}L_{J1}, {}^{(2S+1)}L_{J2} \dots$, the levels having different energies. Inorganic chemists often omit the value of J and refer to a ${}^{(2S+1)}L$ term; we shall usually follow this practice in this book.

To calculate spectroscopic term for a particular configuration:

Suppose we have to calculate term symbol arising from p^2 configuration. As we discussed for p^2 configuration possible L value will be

$L = 2$; corresponds to D state

$L = 1$; corresponds to P state

$L = 0$; corresponds to S state

Since, $m_s = +\frac{1}{2}, -\frac{1}{2}$

Thus, for p^2 case $L = 2, 1, 0, S = 1, 0$

Thus, term arising from p^2 configuration will be $3D, {}^1D, {}^3P, {}^1P, {}^3S, {}^1S$

Now, to write energy state:

i. Write number of possible states using Pauli's exclusion principle:

Figure shown above.

ii. Find the energy state

(a) Take the configuration having maximum M_L

From table it is clear that $M_L = 2$

Maximum M_L value is 2, $M_L = 2$ comes from $L = 2$. Thus, we got D state.

Now take M_S value corresponding to this maximum M_L which is 0, Thus $S = 0$

Thus, spin multiplicity = $2S + 1 = 2 \times 0 + 1 = 1$

Hence energy state corresponding to this particular M_L value = 1D

Number of microstates = $(2L + 1)(2S + 1) = 5$

Thus (2, 0); (1, 0); (0, 0); (-1, 0); (-2, 0) in the table belongs to 1D state.

Now, next possible M_L value is $M_L = 1$

$M_L = 1$ comes from $L = 1$ which corresponds to P state

Corresponding maximum M_S value = 1

Thus, spin multiplicity will be $2S + 1 = 3$

Hence energy state corresponding to this particular M_L value = 3P

Number of microstates corresponding to 3P state = $(2L + 1)(2S + 1) = 9$

Hence, (1, 1), (1, 0), (1, -1), (0, 1), (0, 0), (0, -1), (-1, 1), (-1, 0) and (-1, -1) belong to 3P state.

Next M_L value = 0 thus $L = 0$ which corresponds to S state

Now take M_S value corresponding to this M_L value, which is found to be zero now $S = 0$

Spin multiplicity will be $(2S + 1) = 1$

Hence energy state corresponds to this value is 1S

Number of microstates corresponds to 1S state = $(2L + 1)(2S + 1) = 1$

(0, 0) belongs to 1S state.

From above it is clear that the term arising from p^2 configuration.

i.e. $^3D, ^1D, ^3P, ^1P, ^3S, ^1S$ reduces to $^1D, ^3P, ^1S$ in accordance to Pauli's exclusion principle.

Thus, for p^2 configuration energy state are $^1D, ^3P, ^1S$.

EXAMPLES:

Similarly, we can calculate term symbol arising from any configuration. Now we look in detail at the electronic ground states of atoms with $Z = 1$ to 10.

Hydrogen ($Z = 1$)

A hydrogen atom has an electronic configuration of $1s^1$; for the electron, $l = 0$ so L must be 0 and, therefore, we have an S term.

The total spin quantum number $S = \frac{1}{2}$ so $(2S + 1) = 2$ (a doublet term). The only possible value of J is $\frac{1}{2}$, and so the term symbol for the hydrogen atom is $^2S_{1/2}$.

Helium ($Z = 2$)

For helium ($1s^2$), both electrons have $l = 0$, so $L = 0$. Two electrons both with $n = 1$ and $l = 0$ must have $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$, so $S = 0$ and $(2S + 1) = 1$ (a singlet term).

The only value of J is 0, and so the term symbol is 1S_0 . Thus, the ns^2 configuration, having $L = 0$, $S = 0$ and $J = 0$, will contribute nothing to the term symbol in lithium and later atoms.

The same conclusion can be drawn for any np^6 configuration and the reader is left to confirm this statement.

Lithium ($Z = 3$) and beryllium ($Z = 4$)

Atomic lithium has the electronic configuration $1s^2 2s^1$, and its term symbol is the same as that for hydrogen, $^2S_{1/2}$.

Similarly, the term symbol for beryllium ($1s^2 2s^2$) is the same as that for helium, 1S_0 .

Boron (Z = 5)

For boron ($1s^2 2s^2 2p^1$) we need only consider the p electron. For this, $l = 1$ so $L = 1$ (a P term); $S = \frac{1}{2}$ and so $(2S + 1) = 2$ (a doublet term). J can take values $(L + S); (L + S - 1) \dots |L - S|$, and so

$$J = \frac{3}{2} \text{ or } \frac{1}{2}.$$

The term symbol for boron may be $^2P_{3/2}$ or $^2P_{1/2}$.

Carbon (Z = 6)

For carbon ($1s^2 2s^2 2p^2$), only the p electrons need be considered, and each has $l = 1$. Values of m_l may be +1, 0 or -1, and the algebraic sum of m_l for the individual electrons gives values of $L = 2, 1$ or 0 (D, P or S terms respectively).

As we have derived already, thus for p^2 configuration energy state are $^1D, ^3P, ^1S$.

Nitrogen to Neon (Z = 7 - 10)

A similar treatment for the nitrogen atom shows that the $2p^3$ configuration gives rise to $^4S, ^2P$ and 2D terms.

For the $2p^4$ configuration (oxygen), we introduce a useful simplification by considering it as $2p^6$ plus two positrons which annihilate two of the electrons.

Since positrons differ from electrons only in charge, the terms arising from the np^4 and np^2 configurations are the same.

Similarly, np^5 is equivalent to np^1 .

4.1.4. The angular momentum of an electron

As we already know that, electrons are situated in the orbits that are located around the nucleus. Any electron, in any atom, in any energy state and at any time is not stationary. Thus, the rotating and the revolving electron possess two types of the angular momenta:-

- i. Orbital angular momentum
- ii. Spin angular momentum

i. Orbital angular momentum: -

An electron rotating in its orbital about a nucleus possesses an angular momentum called as *orbital angular momentum*, a measure of which is given by l values corresponding to the orbital. This momentum is quantized and it is usually expressed in terms of the unit, $\frac{h}{2\pi}$, where h is Planck's constant.

$$\text{Orbital angular momentum} = [\sqrt{l(l+1)}] \frac{h}{2\pi}$$

The point to be considered is that, *Orbital angular momentum is a vector quantity*, by which we mean that its direction is important as well as its magnitude. l is always zero or positive and hence so is l .

Now we assume that the energy of a multi-electron species and its orbital angular momentum is determined by a resultant orbital quantum number, L , which is obtained directly from the values of l for the individual electrons; since the orbital angular momentum has magnitude and $(2l + 1)$ spatial orientations (the number of values of m_l), vectorial summation of individual l values is necessary. Since the value of m_l for any electron denotes the component of its orbital angular momentum along the z axis, $m_l(\frac{h}{2\pi})$, algebraic summation of m_l values for individual electrons gives the resultant orbital magnetic quantum number M_L and the component of the resultant orbital angular momentum along the z axis $M_L(h/2\pi)$.

Just as m_l may have the $(2l + 1)$ values $l, (l - 1) \dots 0 \dots -(l - 1), -l$, so M_L may have the $(2L + 1)$ values $L, (L - 1) \dots 0 \dots -(L - 1), -L$, and if, for the multi-electron system, we can find all possible values of M_L , this tells us the value of L .

Energy states for which $L = 0, 1, 2, 3, 4 \dots$ are known as S, P, D, F, G \dots terms respectively, the letters corresponding to s, p, d, f, g \dots used to denote orbitals for which $l = 0, 1, 2, 3, 4 \dots$ in the one-electron case.

The resultant orbital angular momentum is given by:

$$\text{Orbital angular momentum for a multi-electron species} = [\sqrt{L(L + 1)}] \frac{h}{2\pi}$$

ii. Spin angular momentum: -

Every electron in an atom can be considered to be spinning about an axis as well as motion in orbit about the nucleus. Its spin motion is designated by the spin quantum number s which can have a value of $\frac{1}{2}$ only.

$$\text{Spin angular momentum} = [\sqrt{s(s + 1)}] \frac{h}{2\pi}$$

Spin angular momentum is also a vector quantity by which we mean that its direction is important as well as its magnitude.

The resultant spin quantum number, S , denotes the resultant spin angular momentum:

$$\text{Spin angular momentum for a multi-electron species} = [\sqrt{S(S + 1)}] \frac{h}{2\pi}$$

M_S is obtained by algebraic summation of the m_s values for individual electrons. One electron with $s = \frac{1}{2}$ obviously has $S = \frac{1}{2}$ with $M_S = +\frac{1}{2}$ or $-\frac{1}{2}$; M_S for the multi-electron system is analogous to m_s for the one-electron species.

Two electrons lead to $S = 0$ ($m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ giving $M_S = 0$) or $S = 1$ ($m_s = +\frac{1}{2}$ and $+\frac{1}{2}$, or $+\frac{1}{2}$ and $-\frac{1}{2}$, or $-\frac{1}{2}$ and $-\frac{1}{2}$ giving $M_S = 1, 0$ or -1).

In general, for any value of S , there are $(2S + 1)$ values of $M_S : S, (S - 1) \dots 0 \dots -(S - 1), -S$.

Note: The quantity $(2S + 1)$ is the multiplicity of the term where S is the total spin quantum number. Terms for which $(2S + 1) = 1, 2, 3, 4 \dots$ (corresponding to $S = 0, \frac{1}{2}, 1, \frac{3}{2} \dots$) are called singlets, doublets, triplets, quartets and so on.

Total Electronic Angular Momentum:

Finally, we have the resultant inner quantum number, J , also called the total angular momentum quantum number since the total angular momentum is given by:

Total angular momentum for a multi-electron species $= [\sqrt{J(J + 1)}] \frac{h}{2\pi}$ where J is compounded vectorially from L and S , i.e. algebraically from M_L and M_S . Quantum number J can take values $(L + S); (L + S - 1) \dots |L - S|$, the last symbol denoting the modulus of the quantity (i.e. only the magnitude, and not the sign is involved).

Like j for a single electron, J for the multi-electron system must be positive or zero. There are thus $(2S + 1)$ possible values of J for $S < L$, and $(2L + 1)$ possible values for $L < S$. This method of obtaining J from L and S is based on LS (or Russell–Saunders) coupling.

It is the sum of orbital angular momentum and spin angular momentum

$$J = L + S \dots (1)$$

J is the total angular momentum. Since l and s are vectors of orbital angular momentum and spin angular momentum. The equation (1) must be a vector addition.

J can be expressed in terms of total angular momentum quantum number j .

Although it is the only form of coupling of orbital and spin angular momentum that we shall consider in this chapter, it is not valid for all elements (especially those with high atomic numbers). In an alternative method of coupling, l and s for all the individual electrons are first combined to give j , and the individual j values are combined in a $j-j$ coupling scheme (in the inner transition elements).

Spin orbit coupling: -

The coupling of spin angular momentum and the orbital angular momentum is called as the spin orbit coupling. The strength of coupling and its effect on the energy levels of the atom depends on the orientation of both spin and the angular momenta.

There are two different ways as stated in the above part, in which the spin angular momentum and the orbital angular momentum couples are discussed in the following part:

i. Russell Saunders coupling

It is also called as the $L-S$ coupling. It is found in the elements in which the spin orbit coupling is weak, that in the low atomic number entities. Firstly, the individual orbital angular momenta add up to give total orbital angular momentum. And, also, individual spin angular momenta add up to give total spin angular momentum. Then these both total L and S value add up to give the final total angular momentum.

ii. J-J coupling

It is found in the elements in which the spin orbit coupling is large, that in the high atomic number or heavy entities. Firstly, the individual orbital angular momenta couples with the individual spin angular momentum to give individual total angular momentum (J). And, also, individual total angular momenta add up to give total angular momentum (J).

4.1.5. Ground State Term:

i. Hund's Rule

The term derived for a given configuration possess different energies. For example, the term derived for p^2 configuration are 1D , 3P , 1S . These three terms possess different energies. Provided that Russell-Saunders coupling is applicable, the lowest energy term i.e. ground state is summarized in a set of rules known as *Hund's rule*.

There are three important statements of this rule.

- When there is more than one energy state, the energy state having the maximum multiplicity or having most unpaired electron (parallel spins) will have lowest energy i.e. that will be the ground state.
For example, among 1D , 3P , 1S , which are the three-term derived from p^2 configuration, among these three terms, 3P term has highest spin multiplicity, thus it will be the ground state.
- In the case of numerically same multiplicity, then the one with greatest value of L are the most stable and lying at the lower energy level.
For example, in d^2 configuration case out of 3F and 3P , 3F will be the ground state.

- For all terms having a given same multiplicity and L value, the sequence of energy of the components which have different value of J follows the numerical value of J.

(a) If the subshell is less than half filled. The terms which has lowest J value is the ground state. (L-S)

(b) If the subshell is more than half filled. The term which has highest J value will be the ground state. (L+S)

Note: Hund's Rule cannot be used to predict the energy of excited term. Their order can be predicted by quantum mechanical calculation method.

ii. Interpretation of Hund's Rule:

We can focus and understand Hund's first rule. The maximum multiplicity corresponds to the maximum value of S, and this in turn corresponds to the electron spins being preferentially aligned parallel, so favoring a distribution in which the electrons are well separated from one another leading to a low potential energy. Pairing of electrons will lead to lower spin multiplicity. Pairing of electrons, further leads to repulsion between the electrons and therefore higher energy and lower stability.

The way in which the second rule arises is perhaps less easy to visualize; it requires that for the term having the same value of S, the one having the greatest value of L has the lowest energy.

This is clear that, the maximum spins value having connection with the maximum orbital angular momentum, arises when the orbital angular momenta of the individual electrons reinforce each other to the greatest extent. This clearly indicates that the electrons are tending to move in the same direction. One result of this is that they will be in close proximity less often, and will on the whole experience a smaller electrostatic repulsion. The alignment of magnetic moments is a principal factor in the operation of third rule. Where, if the subshell is less than half filled, the state of lowest energy corresponds to the alignment of the orbital magnetic moment antiparallel with the spin magnetic moment so that the value of J given by (L-S) has the lowest value. On the other hand, parallel alignment ($J = L + S$) is the most unfavorable arrangement.

As we importantly mentioned earlier that Hund's Rule cannot be used satisfactorily to predict the order of excited terms. To know which energy state lies above the ground state or what the sequence of energy state is, we have to consider two interaction parameters, which are briefly discussed here.

a. Inter electron repulsion parameter: When the interaction between two or more electrons are considered theoretically, it is possible to write down the energy for each term, which arises as an expression involving several parameters, labeled as F0, F2, F4 etc.

- For p^n configuration the two parameter F0 and F2 are required for d^n F0, F2 and F4 and so on.
- F0 takes account of spherically symmetrical part of electron repulsion, i.e., it involves only the radial functions of the electrons.
- F2 and F4 are connected with the angular dependent electron repulsion.
- Racah recommended the use of two alternative parameters known as Racah B and Racah C parameters, which are related to F parameters by $B = F2 - 5F4$, $C = 35F4$

By doing this he got the energy difference between two energy terms having same multiplicity in the terms of single inter electron repulsion parameter B.

d^2, d^8 ; energy difference between 3F and 3P is $15B$

d^3, d^7 ; $F4 \rightarrow P4 \approx 15B$

d^4, d^6 ; $D3 \rightarrow H3 \approx 12B$

Later it was found that roughly $C \approx 4B$

- v. If in the whole energy level scheme of an atom, we find two terms having identical L and S value e.g. two 2P terms, then the actual energy of the lower one will be depressed and the higher one raised, from their simply calculated values. This is known as **configuration interaction**.

b. Spin orbital coupling parameters:

When spin-orbital coupling is considered, the degeneracy of a given free ion energy term is partly removed, and the energy state is split into two or more components. Consider one electron case for example $p1$ which of course, gives rise to the term 2P . Through spin orbital coupling, two components arise, having $J = 3/2$ and $J = 1/2$.

The energy of each component and the separation between them is expressed in terms of one electron spin orbital coupling parameter $\xi(\text{Zeta})$. There are some quantum mechanical equations are there which are beyond the scope of this book.

4.1.6. Term symbols for closed shell configurations: -

If a subshell is completely filled, such as s^2 , p^6 and d^{10} configurations both L and S are zero. Thus, closed shell always gives 1S_0 term symbol.

Calculation of Ground State Term and Ground State Term Symbol:

Following steps are used for determining the ground state.

- Write the electronic configuration.
- Determine the spin multiplicity ($2S + 1$)
- Determine the maximum possible value M_L
- Select maximum value of J for more than half filled subshell and minimum J value for less than half filled subshell.

a. Ground state term for V^{3+} for d^2 configuration:

$$m_l \quad +2 \quad +1 \quad 0 \quad -1 \quad -2 \quad M_L = +2+1=3$$

↑	↑			
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$\therefore F$ state

$$S = \frac{1}{2} + \frac{1}{2} = 1$$

$$\text{Spin multiplicity } (2S + 1) = 2 \times 1 + 1 = 3$$

$$J = |L + S| \dots\dots\dots |L - S|$$

$$= |3 + 1| \dots\dots\dots |3 - 1|$$

$$= 4, 3, 2$$

$$\text{Ground state term symbol} = {}^3F_2 \quad (\text{for less than half filled subshell } d^2)$$

b. p^3 configuration (Nitrogen atom $\rightarrow 1s^2, 2s^2, 2p^3$)

$$m_l \quad +1 \quad 0 \quad -1 \quad M_L = 0$$

↑	↑	↑
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$\therefore S$ state

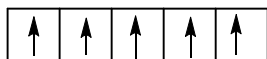
$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$2S + 1 = 2 \times \frac{3}{2} + 1 = 4$$

$$\text{Term} = {}^4S$$

$$\text{For } L = 0, S = 3/2, J = 3/2$$

$$\text{Ground state term symbol} = {}^4S_{3/2}$$

c. Ground state term symbols for high spin d^5s^1 and d^5 configuration:High spin d^5s^1 :
 m_l +2 +1 0 -1 -2 0 $M_L = +2+1+0-1-2+0=0$
 \therefore S state

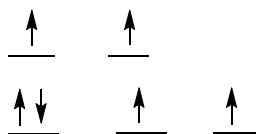
$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 3$$

$$2S + 1 = 2 \times 3 + 1 = 7$$

$$\text{Term} = {}^7S$$

$$\text{For } L = 0, S = 3, J = 3$$

$$\text{Ground state term symbol} = {}^7S_3$$

d. High spin d^6 configuration:

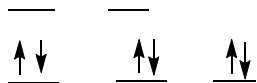
$$S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$$

$$\text{Spin multiplicity } (2S + 1) = 2 \times 2 + 1 = 5$$

$$\text{Maximum value of } M_L = 2+2+1+0-1-2 = 2$$

$$\text{Therefore, } L = 2, \text{ D state}$$

$$\text{Ground state term} = {}^5D$$

e. Low spin d^6 configuration:

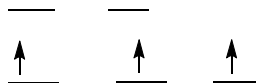
$$S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 0$$

$$\text{Spin multiplicity } (2S + 1) = 2 \times 0 + 1 = 1$$

$$\text{Maximum value of } M_L = 2+2+1+1+0+0 = 6$$

$$\text{Therefore, } L = 6, \text{ I state}$$

$$\text{Ground state term} = {}^1I$$

f. d^3 configuration in the octahedral symmetry:

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

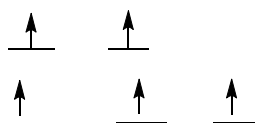
$$\text{Spin multiplicity } (2S + 1) = 2 \times \frac{3}{2} + 1 = 4$$

$$\text{Maximum value of } M_L = 2+1+0 = 3$$

$$\text{Therefore, } L = 3, \text{ F state}$$

$$\text{Ground state term} = {}^4F$$

g. High spin d^5 configuration:



$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{5}{2}$$

$$\text{Spin multiplicity } (2S + 1) = 2 \times \frac{5}{2} + 1 = 6$$

$$\text{Maximum value of } M_L = 2 + 1 + 0 - 1 - 2 = 0$$

Therefore, $L = 0$, S state

Ground state term = 6S

J value for $L = 0$ and $S = 5/2$ is $5/2$

Ground state term symbol ${}^6S_{5/2}$

Table 4.5: Terms arising from p and d configurations

Electronic Configuration	Ground state term	Other term
p^1, p^5	2P	
p^2, p^4	3P	${}^1S, {}^1D$
p^3	4S	${}^2P, {}^2D$
p^6	1S	
d^1, d^9	2D	
d^2, d^8	3F	${}^3P, {}^1G, {}^1D, {}^1S$
d^3, d^7	4F	${}^4P, {}^2H, {}^2G, {}^2F, {}^2D, {}^2P$
d^4, d^6	5D	${}^3H, {}^3G, {}^3F, {}^3D, {}^3P, {}^1I, {}^1G, {}^1F, {}^1D, {}^1S$
d^5	6S	${}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, {}^2G, {}^2F, {}^2D, {}^2P, {}^2S$

4.1.7 Determining Term Symbols

Term symbols for electronic configurations are useful not only to the spectroscopist but also to the inorganic chemist interested in understanding electronic and magnetic properties of molecules. Term symbols are a shorthand method used to describe the energy, angular momentum, and spin multiplicity of an atom in any particular state. The general form is given as aT_j where T is a capital letter corresponding to the value of L (the angular momentum quantum number) and may be assigned as S, P, D, F, G, ... for $|L| = 0, 1, 2, 3, 4, \dots$ respectively.

The superscript "a" is called the spin multiplicity and can be evaluated as $a = 2S + 1$ where S is the spin quantum number.

The subscript "j" is the numerical value of J, a new quantum number defined as: $J = L + S$, which corresponds to the total orbital and spin angular momentum of the system.

Example: The term symbol 3P is read as triplet – P state and indicates that there are two unpaired electrons in a state with maximum orbital angular momentum, $L=1$.

a. M_S and M_L value:

We can define component M_L in two ways.

First, $M_L = m_1 + m_2 + m_3 + \dots$ where m_l corresponds to the l angular momentum quantum number for each electron in a given orientation.

Second, $M_L = L, L-1, \dots, 0, \dots, -L$ where L is the atomic orbital angular momentum. Thus, M_L has $2L + 1$ values.

Similar definitions for M_S , representing the spin of the system may be made with allowable values of $M_S = 2S+1$. The total angular momentum quantum number, J , is given as $J = L+S, L+S-1, \dots, |L-S|$. It is the absolute magnitude of J that determines the total angular momentum.

4.1.8. Calculation of ground term symbol:

It is relatively easy to calculate the term symbol for the ground state of an atom using Hund's rules. It corresponds with a state with maximum S and L .

1. Start with the most stable electron configuration. Full shells and subshells do not contribute to the overall angular momentum, so they are discarded.

If all shells and subshells are full then the term symbol is 1S_0 .

2. Distribute the electrons in the available orbitals, following the Pauli exclusion principle. First, fill the orbitals with highest m_l value with one electron each, and assign a maximal m_s to them (i.e. $+\frac{1}{2}$). Once all orbitals in a subshell have one electron, add a second one (following the same order), assigning $m_s = -\frac{1}{2}$ to them.

3. The overall S is calculated by adding the m_s values for each electron. According to Hund's first rule, the ground state has all unpaired electron spins parallel with the same value of m_s , conventionally chosen as $+\frac{1}{2}$. The overall S is then $\frac{1}{2}$ times the number of unpaired electrons. The overall L is calculated by adding the m_l values for each electron (so if there are two electrons in the same orbital, add twice that orbital's m_l).

4. Calculate J as

- if less than half of the subshell is occupied, take the minimum value $J = |L - S|$;
- if more than half-filled, take the maximum value $J = L + S$;
- if the subshell is half-filled, then L will be 0, so $J = S$.

Examples:**1. The ground state term symbols corresponding to d^7 :**

d^7 electron configuration can be written as follows:

+2 +1 0 -1 -2



A) Here S value can be calculated as $(2s+1) = (2 \times 3/2 + 1) = 4$

B) For L values,

L =	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	...
	S	P	D	F	G	H	I	K	L	M	N	O	Q	R	T	U	V	

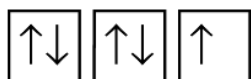
$L = 2(2) + 1(2) + 0 - 1 - 2 = 3$, which is "F" in spectroscopic notation.

C) For J value, In this case, it is more than half filled, take the maximum value $J = L + S$

Thus, d^7 electron configuration has a ground-state term symbol of $^4F_{9/2}$.

2. The ground state term symbols corresponding to p^4 : p^4 electron configuration can be written as follows:

+1 0 -1



A) Here S value can be calculated as $(2s+1) = (2 \times 1+1) = 3$

B) $L = 2(1) + 0 - 1 = 1$, which is "P" in spectroscopic notation.

C) For J value, In this case, it is more than half filled, take the maximum value $J = L + S = 1+1 = 2$

Thus, p^4 electron configuration has a ground-state term symbol of 3P_2 .

3. The ground state term symbols corresponding to p^3 :

p^3 electron configuration can be written as follows:



A) Here S value can be calculated as $(2s+1) = (2 \times 3/2+1) = 4$

B) $L = 1 + 0 - 1 = 0$, which is "S" in spectroscopic notation.

C) For J value, In this case, it is more than half filled, take the maximum value $J = 0$

Thus, p^3 electron configuration has a ground-state term symbol of 4S_0 .

4. The ground state term symbols corresponding to d^3 :

d^3 electron configuration can be written as follows:



A) Here S value can be calculated as $(2s+1) = (2 \times 3/2+1) = 4$

B) $L = 2 + 1 - 0 = 3$, which is "F" in spectroscopic notation.

C) For J value, In this case, it is less than half filled, take the maximum value $J = L - S = 3/2$

Thus, d^3 electron configuration has a ground-state term symbol of $^4F_{3/2}$.

5) The ground state of V^{3+} ion is:

V^{3+} corresponds to d^2 system and d^2 electron configuration can be written as follows:



A) Here S value can be calculated as $(2s+1) = (2 \times 1+1) = 3$

B) $L = 2 + 1 = 3$, which is "F" in spectroscopic notation.

C) For J value, In this case, it is less than half filled, take the maximum value $J = 2$

Thus, d^2 electron configuration has a ground-state term symbol of 3F_2 .

6. Ground term of the of Cr^{3+} is:

Cr^{3+} corresponds to d^3 system and d^3 electron configuration can be written as follows:



A) Here S value can be calculated as $(2s+1) = (2 \times 3/2+1) = 4$

B) $L = 2 + 1 - 0 = 3$, which is "F" in spectroscopic notation.

C) For J value, in this case, it is less than half filled, take the maximum value $J = L - S = 3/2$

Thus, Cr^{3+} has a ground-state term symbol of ${}^4F_{3/2}$.

4.1.8 Trick To Find All The Possible Terms Of A Given Configuration:**a. p^1d^1 configuration:**

As we have already discussed, for an p^1d^1 configuration, the total number of microstates will equal the product of the microstates for these individual orbitals.

Thus, microstates of an p^1d^1 configuration, microstates = 6 (from p^1) \times 10 (from d^1) = 60.

We know that, $L=1$ for P and $L=2$ for D term.

Thus, $|L \text{ for P} + L \text{ for D}| = 1+2 = 3$

$|L \text{ for P} - L \text{ for D}| = |1-2| = 1$

Possible terms can take the values from $|L \text{ for P} + L \text{ for D}|$ to $|L \text{ for P} - L \text{ for D}|$.

Now, we will arrange all possible term symbols this into small table for better understanding.

\downarrow S value / L value \rightarrow	1	2	3
S=0 (Singlet)	1P	1D	1F
S=1 (Triplet)	3P	3D	3F

Possible terms of the p^1d^1 configurations: 1P , 1D , 1F , 3P , 3D and 3F

This can be cross-checked by assigning the multiplicities:

Term	Multiplicity
1P	3
1D	4
1F	7
3P	9
3D	15
3F	21
p^1d^1	60

Key point: To calculate the meaningful terms, Cancel the odd term if $S=0$ and cancel the even term if $S=1$

\therefore We get, $S=0$ (Singlet) terms as 1D and $S=1$ (Triplet) terms as 3P and 3F

Thus, meaningful terms for p^1d^1 configurations are 1D , 3P and 3F

4.2. Electronic Spectra of the Coordination Complexes

4.2.1. Lambert Beers Law:

The Beer-Lambert law may be used to describe the absorption of light (ignoring scattering and reflection of light from cell surfaces) at a given wavelength by an absorbing species in solution:

$$\log \frac{I_0}{I} = A = \epsilon l c$$

where **A = absorbance**

ϵ = molar absorptivity coefficient {L/mol.cm}

l = path length of the solution in cm

C = concentration of the absorbing species

Absorbance is a dimensionless quantity. An absorbance of 1.0 corresponds to 90% absorption at a given wavelength, an absorbance of 2.0 corresponds to 99% absorption and so on. Spectrophotometers commonly obtain spectrum as plots of absorbance versus wavelength. The molar absorptivity is a characteristic of the species that is absorbing the light and is highly dependent on wavelength. A plot of molar absorptivity versus wavelength gives a spectrum characteristic of the molecule or ion in question.

As we will see, this spectrum is a consequence of transitions between states of different energies and can provide valuable information about those states and in turn, about the structure and bonding of the molecule or ion. Although the quantity most commonly used to describe absorbed light is the wavelength, energy and frequency are also used. In addition, as we have already stated, the wave number the number of waves per centimeter, a quantity proportional to the energy, is frequently used.

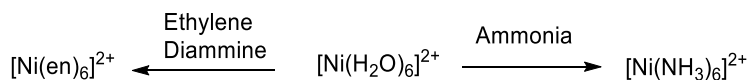
4.2.2. BASICS:

Most of the d block complexes are colored in the solid as well as in the solution state. This is somewhat different from the s and p block elements which are almost white in color. The transition metal complexes have colors that originate from the absorption of the visible light by them. The science behind that: Electromagnetic spectrum of white light consists of the continuous spectrum of the wavelengths or wave number corresponding to the different colors. If a compound absorbs the light of one color, then it emits the complimentary color of the absorbed one. For example, if any compound is absorbing the light in the spectrum of the orange color, it will emit the blue color. This blue color attacks to retina of our eye and *the compound appears blue in color*. A compound appears blue only if it absorbs the wavelengths of all colors and transmits the blue one only. A compound appears black if it absorbs all the radiations of the white light in the visible region. If there is no absorption, the compound appears white or colorless. Most of the complexes are colored due to this absorption – emission phenomenon. This absorption and emission depend upon the metal and ligand bonding, metal electron configuration and the mainly, crystal field theory. Following table shows the different colors of the different complexes

Table 4.6: The different colors of the different complexes

Complex	Color
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Purple
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	Pink
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Blue
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Violet
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	Blue
$[\text{Co}(\text{Cl})_4]^{2-}$	Blue
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	Green
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Blue
$[\text{Ni}(\text{en})_6]^{2+}$	Violet

It is observed that: -



Complementary colors can conveniently be remembered as the color pairs on opposite sides of the color wheel shown below:

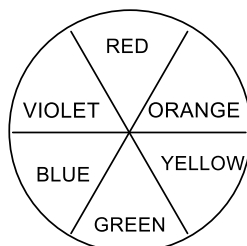


Figure 4.1: Colour wheels of principal colours

Thus, For example, when white light (containing a broad spectrum of all visible wavelengths) passes through a substance that absorbs red light, the color observed is green. Green is the complement of red, so green predominates visually when red light is subtracted from white.

An example from coordination chemistry is the deep blue color of aqueous solutions of copper (II) compounds, containing the ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. The blue color is a consequence of the absorption of light between approximately 600 and 1000 nm (maximum near 800 nm), in the yellow to infrared region of the spectrum. The color observed which is blue, is the average complementary color of the light absorbed.

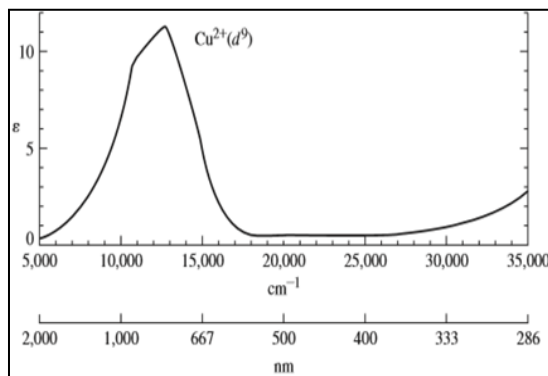


Figure 4.2: Spectra for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

Although it looks so simply that the complementary color will give the idea of the absorbed color, it is not that much simple! It is not always possible to make a simple prediction of color directly from the absorption spectrum, in large part because many coordination compounds contain two or more absorption bands of different energies and intensities. *The net color observed is the color predominating after the various absorptions are removed from white light.*

4.2.3. Spectral features

In the coordination complexes, the color to the compound is observed due to the electronic transition from the lower energy level to the higher energy level by the absorption of the light. When photon of the suitable wavelength which is equal to the energy difference between the excited state and the ground state of the system is incident on the electron present in the ground state, that particular electron(s) absorb that energy and gets *excited* to the higher energy level. This process of the excitation of an electron is called as the *electronic transition*. In the case of the octahedral complexes, t_{2g} is the ground state and e_g is the excited state. Thus the transition takes place from the t_{2g} orbitals to the e_g orbitals. In case of the tetrahedral complexes, e is the ground state energy level and t_2 is the excited state energy level thus the electronic transition takes place from e to t_2 . As these are the energy states obtained after the removal of the degeneracy, collectively they are called as the *d orbitals* and the transition taking place in them are called as the *d-d transitions*.

